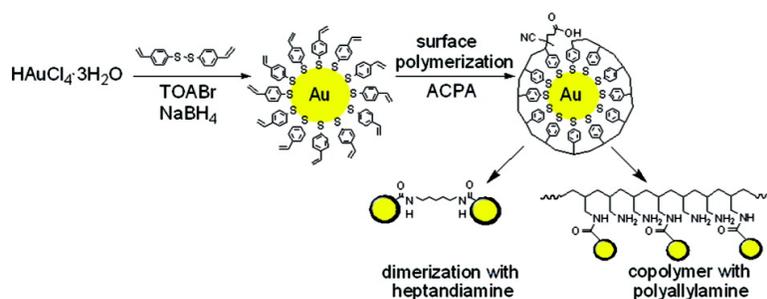


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Stoichiometric Functionalization of Gold Nanoparticles in Solution through a Free Radical Polymerization Approach

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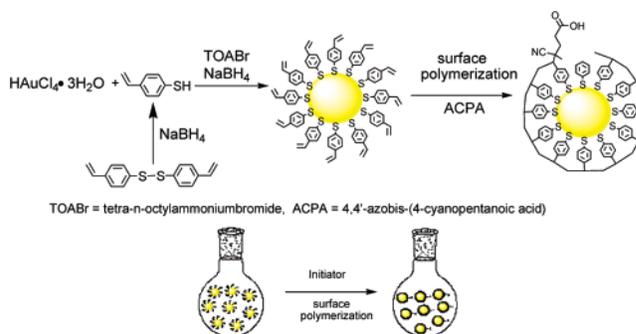
A wealth of literature is known for the preparation and functionalization of nanoparticles,¹ nanofibers,² and nanotubes such as carbon nanotubes.³ Despite these accomplishments controlled functionalization is still a challenge. Controlled functionalization on the surface of nanomaterials would open completely new perspectives in new materials synthesis, nanomaterials orientation, and new properties generation. However, until now there are only few reports of nanoparticles with well-defined stoichiometrical functionality. Dendritic nanoparticle structures were the first nanomaterials with a precise stoichiometrical functionalization as the stoichiometries are mathematically defined by geometric restrictions.⁴ These precise stoichiometries were already used to synthesize defined hybrid materials.⁵ Later Feldheim et al. prepared dimers of gold nanoparticles by ligand exchange reactions of citrate-capped gold nanoparticles with dithiols.⁶

The first example of stoichiometrical monofunctionalized gold clusters was reported to the best of our knowledge in 2000 by Hainfeld et al.⁷ Afterward, Zanchet et al. managed to separate gold nanoparticles with a defined number of DNA strands by gel electrophoresis.⁸ Another important step toward gold nanoparticles with stoichiometrical functionalization was accomplished by Worden et al.⁹ via a solid-phase chemistry method. In the latest concept developed by Lévy et al.¹⁰ peptide-labeled gold nanoparticles were separated by immobilized metal ion affinity chromatography according to the number of peptides on the nanoparticle surface.

In this contribution a new highly versatile route for the stoichiometrical functionalization of nanoparticles by surface polymerization is presented exemplarily for gold nanoparticles. The functionalization of gold nanoparticles by a single carboxyl group is described and proven by chemical linkage of pairs of gold nanoparticles and the preparation of ordered arrays of gold nanoparticles. The concept of stoichiometrical functionalization is shown in Scheme 1. Radically polymerizable vinyl groups were immobilized on the surface of gold nanoparticles by 4-vinylthiophenol moieties. Subsequently functionalized radical initiators were employed leading to the polymerization of vinyl groups within individual nanoparticles and the immobilization of the initiator functionality. 4-Vinylthiophenol-stabilized gold nanoparticles were prepared in a similar fashion to the well-known Brust–Schiffrin procedure¹¹ with 1,2-bis(4-vinylphenyl)disulfane as thiol precursor for the labile 4-vinylthiophenol.

Reduction with NaBH₄ in this procedure both led to the formation of gold nanoparticles and 4-vinylthiophenol at the same time.¹² Synthesis of the thiol precursor was accomplished by a reaction sequence starting from 4-bromothiophenol shown in the supplement. TEM investigations of these gold nanoparticles revealed particles between 2 and 5 nm without aggregates. In accordance with other reports¹³ on arenethiolate-stabilized gold nanoparticles our particles showed typical properties of arenethiolate-stabilized gold nanoparticles such as insolubility in *n*-hexane. 4-Vinylthiophenol-stabilized

Scheme 1. Synthetic Procedure



gold nanoparticles were isolated as a black powder together with the phase transfer catalyst TOABr through solvent removal under reduced pressure.

To accomplish the polymerization of vinyl groups the nanoparticles were dispersed in THF and the degassed dispersion was polymerized with the initiator 4,4'-azobis-(4-cyanopentanoic acid) at 80 °C in an oil bath for 8 h. Complete polymerization of vinyl groups was indicated by the disappearance of the vinyl-group signals in ¹H NMR spectra. The polymerization was run with a typical concentration ratio of 190 mg nanoparticles versus 0.3 mL of a 0.735 mmol/l initiator solution. No agglomeration occurred during surface polymerization—even if higher initiator to particle ratios were used. TEM after the surface polymerization showed no formation of dimers or oligomers. After the polymerization procedure the functionalized gold nanoparticles were isolated by evaporation of solvent under reduced pressure and purified by dispersing them in MeOH followed by centrifugation for at least three times.

Loading of the gold nanoparticles with the carboxylic initiator moiety was determined according to a procedure of Worden et al.⁹ According to this procedure 1,7-heptandiamine and diisopropylcarbodiimide were added leading to the formation of amide functions from the carboxylic acid group. In the case of only one carboxylic acid group, the coupling reaction will lead to dimers. In contrast, nanoparticles bearing more than one carboxylic acid group will form higher order nanoparticles structures like trimers, tetramers, and even larger aggregates. During coupling no aggregation occurred and dimers together with nonfunctionalized nanoparticles were observed in TEM (Figure 1) whereas when nanoparticles were polymerized with a seventeen-fold higher amount of initiator all nanoparticles precipitated out within a few minutes. Counting of gold nanoparticles on larger sections on a TEM grid gave a total of 419 particles of those 255 (61%) were single particles, 146 (35%) formed dimers, and 18 (4%) formed trimers. TEM analysis also showed that the size of gold nanoparticles did not change during the polymerization process and coupling procedure, proving that there were no side reactions or unwanted

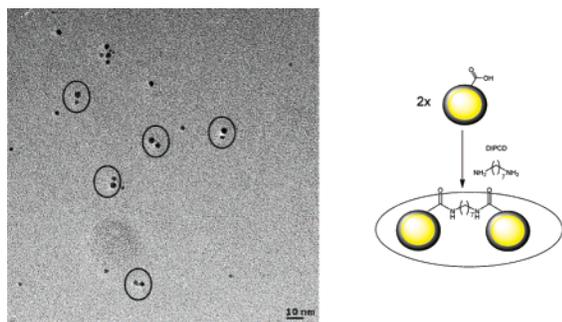


Figure 1. Dimerization after coupling with 1,7-heptandiamine.

fusion of gold nanoparticles.¹⁴ The recently published X-ray data of gold nanoparticles by Jadzinsky et al.¹⁵ support the assumption of a relative dense and clear defined 4-vinylthiophenol shell on the particles. A defined monomer shell is essential for a controlled surface polymerization process.

As free radical polymerizations are generally thought to be relatively uncontrolled processes, there must be some factors inducing control in our surface polymerization of gold nanoparticles. One factor inducing control is the presence of cationic TOABr molecules. It is well-known from literature that cationic molecules like TOABr are easily incorporated in the ligand shell of gold nanoparticles,¹⁶ leading to positively charged nanoparticles. Due to repulsive forces between the charged particles, polymerization does not lead to agglomeration, even in the case that more than one initiator moiety is bound to a single particle. Additionally, repulsion of gold nanoparticles are likely to hinder transfer reactions between different particles. A second factor inducing control is the time frame of the polymerization process. Whereas polymerization is a fast process, initiator decomposition is a slow process. Therefore, it is unlikely that two radicals start polymerization on the same particle within a given time frame. In our case this time frame is determined by the decomposition rate of our initiator, which was determined to be $1.91 \times 10^{-5} \text{ s}^{-1}$ at 65 °C in dioxane¹⁷ corresponding to a half-life time of approximately 10 h.

The availability of stoichiometrically functionalized nanoparticles enabled us to prepare a novel nanoparticle/polymer copolymer from polyallylamine and monofunctionalized nanoparticles. The particles were dispersed in DMF and a solution of polyallylaminehydrochloride with a M_w of 15 000 in DMF, diisopropylcarbodiimide and 1,8-diazabicyclo[5.4.0]undec-7-ene were added. Stirring at room temperature led to the formation of amide functions between the nanoparticles and polymeric amino groups liberated from its hydrochloride salt by the basic 1,8-diazabicyclo[5.4.0]undec-7-ene. The nanoparticle/polymer copolymer could be precipitated by addition of Et₂O. The purified precipitate was highly soluble in water, showing that the monofunctionalized gold nanoparticles had become water soluble by attaching to a water soluble polymer. TEM inspections (Figure 2) revealed the chainlike structure of these nanoparticle/polymer copolymers. Therefore covalent attaching of stoichiometrically functionalized nanoparticles on polymers can be seen as a new way to stain polymer chains for electron microscopy and could bring some new insight views in the conformity of polymers. Moreover our nanoparticle/polymer copolymer is a clear approach to generate new defined nanostructures. In another recent example DeVries et al.¹⁸ used stoichiometric functionalized gold nanoparticles as “nanoparticle monomers” and “polymerized” them through coupling with a bifunctional amine into chains of more than a dozen units.

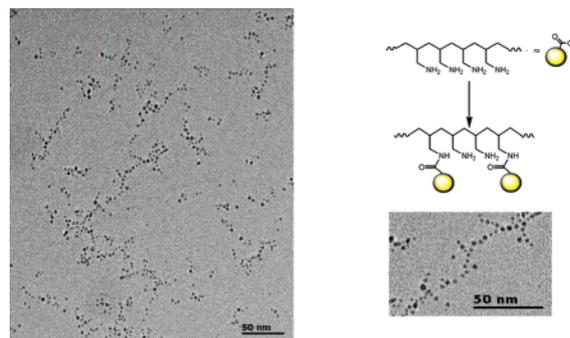


Figure 2. Ordered arrays of gold nanoparticles.

With the surface polymerization of nanoparticles stabilized by a vinyl monomer a fundamental new concept leading to stoichiometric functionalized nanoparticles was developed. Extension of this concept to emulsion polymerizations and to other vinyl-stabilized nanoparticles like TiO₂ nanoparticles stabilized with methacrylate containing moieties are under way. The broad availability of stoichiometrically functionalized nanoparticles will enable the preparation and investigation of a novel class of hybridmaterials such as nanoparticle/polymer copolymers just as shown here and will certainly provide novel materials with new sets of structure–property relationships.

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Supporting Information Available: Experimental details for synthetic procedures, characterization, and additional TEM pictures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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