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Alternative preparation of size-controlled thiol-capped gold colloids

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Abstract Colloidal nanoparticles find application in chemistry, biology, and life science. We report an alternative preparation method for thiol-capped gold colloids by leaching of premade particles on a support. Via this method, monodispersed particles in the size of 2 to 2.5 nm can be obtained whereas the occurrence of bigger particles is restricted.

Keywords Gold · Colloid · Nanoparticle · Thiol-capped

An increasing interest in colloidal nanoparticles developed over the past years as an ever-growing number of applications in chemistry, biology, and life science emerged [1]. In biology and life science, these colloids are used for labeling [2], (drug) delivery [3], heating [4], and sensing [5] whereas supported [6] or unsupported [7] nanoparticles in chemistry are used especially in the field of catalysis. Although numerous preparation methods for colloidal nanoparticles exist [8–10], scientists still look for alternative routes as the demand for small monodispersed nanoparticles in solution is high. The challenge in the preparation of colloid gold nanoparticles is the size control especially in the regime below 5 nm as gold tends to sinter easily. Gold colloids are typically synthesized through reduction of a gold precursor in solution. We propose an alternative preparation method which yields monodispersed organic thiol-capped gold colloids in the size of 2 to 2.5 nm and prevents the occurrence of nanoparticles bigger than 5 nm.

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The method is based on the leaching of premade particles that are attached to a support. Because of the ability to control the gold particle size in supported gold [10], the method provides new opportunities to synthesize gold colloids of well-defined size.

The gold colloids were obtained from Au/Al_2O_3 colloid precursors which were prepared by a deposition precipitation with urea method according to [11]. The Au/Al_2O_3 colloid precursor and the colloid were characterized by transmission electron microscopy (TEM), atomic absorption spectroscopy, and high-energy resolution fluorescence-detected X-ray absorption spectroscopy (HERFD XANES). All experimental details of Au/Al_2O_3 colloid precursor synthesis, colloid preparation, and characterization can be found in the supplementary information. In short, a suspension of the Al_2O_3 support, urea, and an appropriate amount of $HAuCl_4 \cdot 3H_2O$ in water was prepared and stirred at 80 °C for 16 h under the exclusion of light. The powder was filtered, washed three times with water, and dried in vacuum overnight. After pretreatment in a flow of 5 % H_2/He at 300 °C, the Au/Al_2O_3 precursor was mixed with the corresponding organic thiol in degassed (with N_2) ethanol at a molar Au/thiol ratio of 1/20 for 16 h. After that, the catalyst was filtered, washed three times with EtOH, and dried in vacuum overnight. We refer to the 1-dodecanethiol-capped Au/Al_2O_3 colloid precursor as "Au_{C12}/Al_2O_3" in the following. The gold colloid was obtained by heating Au_{C12}/Al_2O_3 in toluene at the corresponding temperature. We refer to the 1-dodecanethiol-capped gold colloid as "Au_{C12} colloid" in the following.

The transition of the gold nanoparticles from the Al_2O_3 support to the liquid phase is visualized in Fig. 1. Figure 1 shows a characteristic TEM picture of Au_{C12}/Al_2O_3 before and the Au_{C12}/Al_2O_3 and the liquid toluene phase after heating in toluene at 80 °C.

Before heating in toluene, the thiol-capped Au nanoparticles were monodispersed and widely distributed on the Al_2O_3 support with a mean particle size of 2.8 nm.
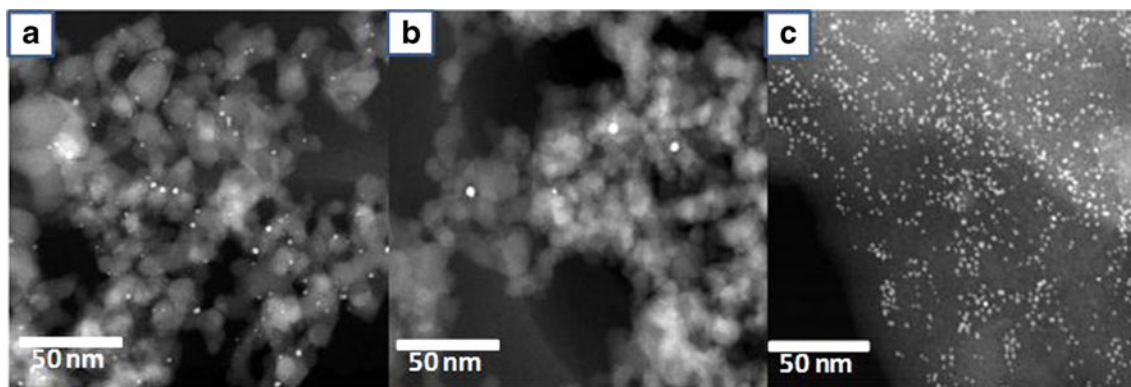
Fig. 1 Characteristic TEM picture of Au_{C12}/Al_2O_3 before (**a**) and after (**b**) heating at 80 °C in toluene and the liquid phase after heating at 80 °C

After heating, the Al_2O_3 support showed only residual big nanoparticles (>5 nm) on the surface of the Al_2O_3 support whereas all smaller sized nanoparticles had disappeared. These particles were found in the toluene phase which turned from colorless to dark red, because of the gold colloid. The mean particles size was 2.7 nm suggesting, combined with the HERFD XANES data (supplementary information), that the gold nanoparticles leached into the liquid toluene phase as a whole. We investigated the effect of temperature on the colloid. Figure 2 shows the particle size distribution (left) and a characteristic TEM picture (right) of the Au_{C12} colloid after heating at 80 °C (a) and 100 °C (b) in toluene.

The particle size distribution obtained by heating the Au_{C12}/Al_2O_3 catalyst in toluene at 80 °C (a) resulted in a Gaussian shape with a maximum at 2.2 nm. The characteristic TEM picture shows spherical monodispersed gold nanoparticles of the same size. Heating the Au_{C12}/Al_2O_3 at 100 °C (b) in toluene resulted also in spherical Au_{C12} nanoparticles with a Gaussian particle size distribution, but much narrower compared to (a). The maximum was located at 1.8 nm. Additionally to the temperature effect, we investigated the effect of the molar Au/S ratio during the Au_{C12}/Al_2O_3 treatment and subsequent heating at 80 °C on the resulting Au_{C12} colloid. Table 1 summarizes the effect

Fig. 2 Particle size distribution (*left*) and characteristic TEM image (*right*) of the Au_{C12} colloid after heating at **a** 80 °C and **b** 100 °C
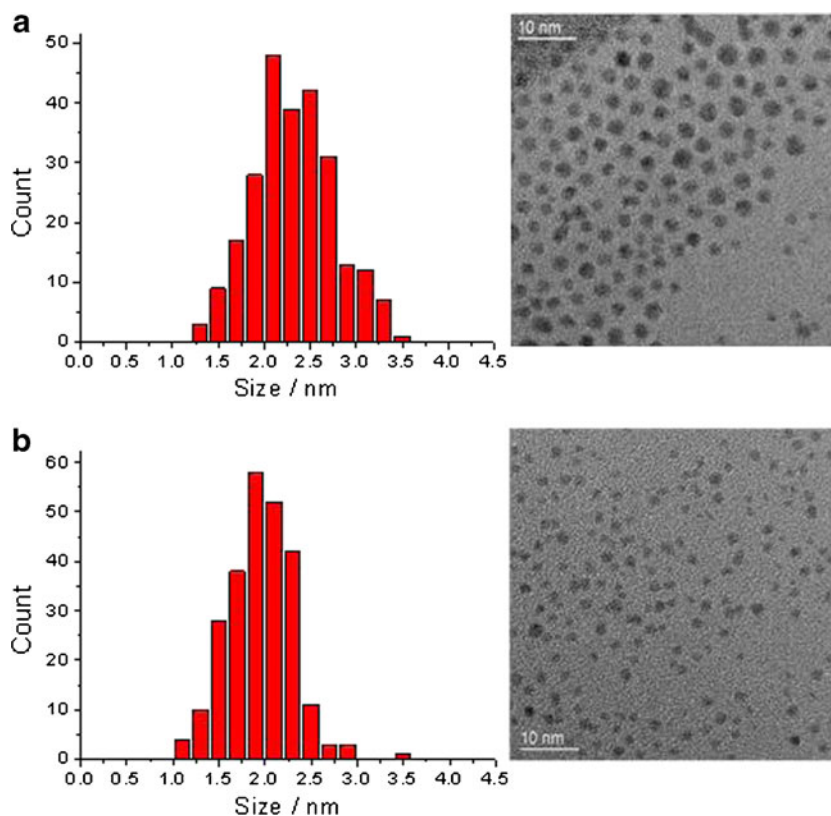
Table 1 Dependence of Au/S ratio on Au colloid yield for the Au$_{C12}$ colloid after heating the Au$_{C12}$/Al$_2$O$_3$ colloid precursor in toluene at 80 °C

Molar Au/S ratio	Au colloid yield (%)
1:20	66.9
10:1	33.2
25:1	6.2
50:1	–
75:1	–

Table 2 Dependence of organic thiol on Au colloid yield after heating in toluene at 80 °C

Thiol	Au colloid yield (%)
1-Octadecanethiol	78.5
1-Dodecanethiol	66.9
1-Propanethiol	62.5
1,6-Hexanedithiol	11.5
1-Thioglycerol	7.3

**Table 3** Dependence of solvent on Au colloid for the Au$_{C12}$ colloid yield after heating in toluene at 80 °C

Solvent	Au colloid yield (%)
n-Hexane	74.6
Toluene	66.9
Ethanol	24.5
Water	23.4

on the yield of Au$_{C12}$ colloid for different molar Au/S ratios of the Au$_{C12}$/Al$_2$O$_3$ colloid precursor.

Whereas no effect on the particle size was observed, we found that the gold colloid yield in toluene strongly depended on the molar Au/S ratio during the preparation of the Au$_{C12}$/Al$_2$O$_3$ colloid precursors. Whereas no leaching was observed for Au/S ratios of 75:1 and 50:1, gold nanoparticles were transferred to the liquid phase starting at ratios of 25:1. Higher gold colloid yields could be achieved via the application of different organic thiols, without affecting the size (Table 2). The maximum amount of gold that could be brought into solution was almost 80 %, which is likely because the bigger nanoparticles remain on the Al$_2$O$_3$ support as observed in Fig. 1b.

In general, thiols with a similar polarity as the solvent toluene (1-propanthiol, 1-dodecanethiol, 1-octadecanethiol) yielded higher gold colloid concentration, whereas thiols with an adjacent polar group resulted in lower concentrations. Within a row of the unpolar thiols, a longer CH$_3$(C$_n$H$_{2n}$) chain yielded a higher gold colloid concentration with a maximum of 78.5 % observed for 1-octadecanethiol in toluene. The same trend was observed within the polar thiols. A similar tendency was observed for the preparation of the Au$_{C12}$ colloid in different solvents (Table 3).

The gold colloid yield strongly depended on the solvent used during preparation: the more polar the solvent and thus the more interaction of the CH$_3$(CH$_2$)$_{12}$ chain with the solvent, the higher the gold colloid yield. The maximum Au$_{C12}$ colloid yield was obtained in the most unpolar solvent, n-hexane, whereas as much as 50 % less was observed in the most polar solvent, water. According to these observations, we propose a model for the fabrication of the size-controlled thiol-capped gold nanoparticles as depicted in Scheme 1.

Scheme 1 Schematic representation for the formation of thiol-capped gold nanoparticles
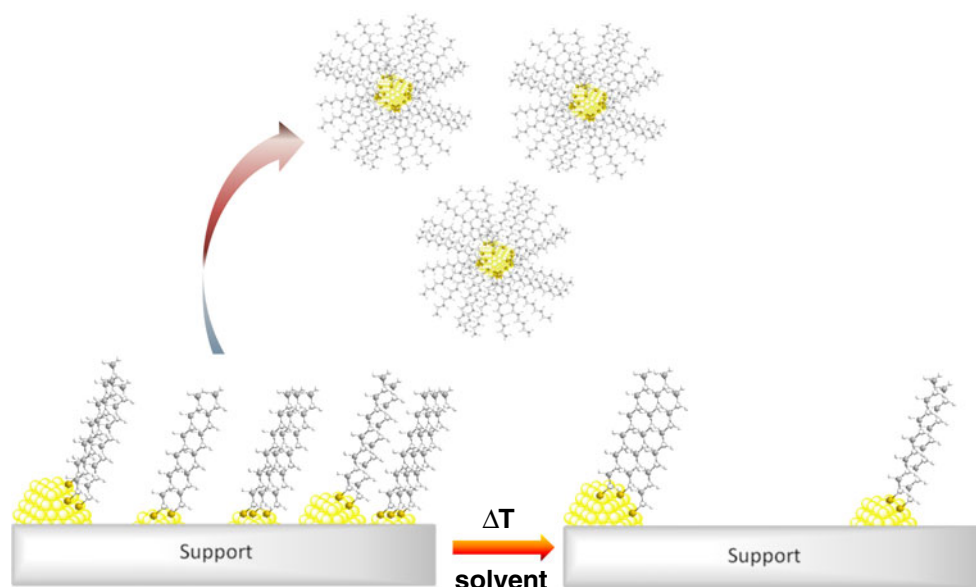
Due to the interaction of the long $CH_3(C_nH_{2n})$ chains with the solvent, the organic thiol-capped nanoparticles are transferred to the liquid phase in the same structure as they had on the support. The better the interaction between the organic thiols and the solvent, the higher the Au colloid yield, whereas this interaction is not strong enough to rip of particles bigger than 5 nm.

To summarize, we showed that monodispersed thiol-capped gold colloids in the range of 2 to 2.5 nm can be synthesized by initial treatment of Au/Al_2O_3 colloid precursors with organic thiols and subsequent heating in a solvent. Size control during preparation is given as particles bigger than 5 nm remain on the Al_2O_3 surface whereas all smaller sizes are transferred to the liquid phase. Variation of colloid precursor treatment and extraction temperature enables fine tuning of particle size whereas the yield of the gold colloid can be maximized via the right combination of organic thiol and solvent. This new route opens a new horizon for the production of colloidal particles in the size range below 5 nm.

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