

Seed-mediated synthesis of gold nanorods: control of the aspect ratio by variation of the reducing agent

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Received: 5 November 2012 / Accepted: 25 January 2013 / Published online: 9 February 2013
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Abstract Seed-mediated growth methods involving reduction of tetrachloroaurate(III) with ascorbic acid are common for the synthesis of gold nanorods. This study shows, however, that simply by appropriate choice of the reducing agent a drastic influence on the aspect ratio can be attained. Weaker reducing agents, such as dihydroxybenzene isomers (hydroquinone, catechol or resorcinol) or glucose can increase the aspect ratio of the nanorods by an order of magnitude, up to values as high as 100 (nanowires). The increase in aspect ratio is mainly a consequence of an increase in length of the particles (up to 1–3 μm). This effect is probably associated with a decrease in the reduction rate of gold(III) species by dihydroxybenzenes or glucose compared to ascorbic acid. The reduction potential of the reducing agents strongly depends on the pH value, and related effects on the dimensions of the nanoparticles are also reflected in this study. The nanorods exhibited penta-twinned nature without noteworthy defects (e.g. stacking faults and dislocations).

Keywords Gold · Nanorods · Seed-mediated growth method · Ascorbic acid · Dihydroxybenzenes · Glucose · Nanowires

Introduction

During the last decades gold nanorods have attracted considerable attention (Busbee et al. 2003; Chang et al. 1999; Gao et al. 2003; Garg et al. 2010; Jana et al. 2001a, b; Jiang et al. 2006; Jiang and Pileni 2007; Kang et al. 2003; Keul et al. 2008; Kim et al. 2002; Liu et al. 2004; Liu and Guyot-Sionnest 2005; Martin 1996; Nikoobakht and El-Sayed 2003; Park et al. 2006; Pérez-Juste et al. 2004; Sau and Murphy 2004, 2007; Smith and Korgel 2008; Smith et al. 2009; Wirtz et al. 2002; Wu et al. 2007; Yacamán et al. 2001; Yu et al. 1997) due to their unique size- and shape-dependent properties (Pérez-Juste et al. 2005; El-Sayed 2001). Various approaches to synthesize this kind of particle morphology have been developed, such as electrochemical (Chang et al. 1999; Yu et al. 1997), photochemical (Kim et al. 2002; Esumi et al. 1995) or template-based methods (Martin 1996; Wirtz et al. 2002), microwave rapid heating (Liu et al. 2004) and the seed-mediated growth method (Busbee et al. 2003). In particular, the latter—which was first introduced by Murphy and co-workers in 2001 (Jana et al. 2001a)—was in the focus of various studies (Busbee et al. 2003; Gao et al. 2003; García et al. 2011; Garg et al. 2010; Grzelczak et al. 2008; Jiang et al. 2006; Jiang and Pileni

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2007; Kang et al. 2003; Keul et al. 2008; Liu and Guyot-Sionnest 2005; Nikoobakht and El-Sayed 2001; Park et al. 2006; Pérez-Juste et al. 2004; Sau and Murphy 2004; Smith and Korgel 2008; Wu et al. 2007). The basis of all modified seed-mediated growth procedures is the addition of a certain amount of small gold colloids (a so-called seed solution) to a so-called growth solution containing a surfactant (typically cetyltrimethylammonium bromide (CTAB)), a gold salt (e.g. $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$) and ascorbic acid as a reducing agent. Hereby, two different approaches of the seed-mediated growth method have to be considered: with and without the addition of silver nitrate. The addition of a small amount of silver nitrate to the growth solution commonly leads to a high yield of short aspect ratio nanorods (aspect ratio between 2 and 3) (Garg et al. 2010; Jiang et al. 2006; Jiang and Pileni 2007; Keul et al. 2008; Liu and Guyot-Sionnest 2005; Nikoobakht and El-Sayed 2001; Sau and Murphy 2004; Smith and Korgel 2008; Grzelczak et al. 2008; García et al. 2011), while the synthesis of gold nanorods without silver nitrate commonly yields higher aspect ratios (5–23), however, in a relatively low yield (Jana et al. 2001a; Kang et al. 2003). That means, besides rods also other shapes such as spherical particles and triangular prisms emerge in the latter situation and thus, a particle separation process has to be applied after the synthesis (Koepl et al. 2012). Also, reproducibility has often been a major problem. These drawbacks were eliminated lately by modification of the synthesis method (Koepl et al. 2011) and a centrifugation procedure (Park 2006) to separate the gold nanorods from spherical particles (Koepl et al. 2012).

Recently, we reported that the substitution of H_2O by D_2O as a solvent led to a pronounced increase in aspect ratio of gold nanorods, mainly caused by an increase of nanorods length while the width remained in the same size range (Koepl et al. 2012). Most likely, a H/D exchange at ascorbic acid results in a decrease of the reduction rate of gold(III) species. This implies that an O–H (or O–D) bond is involved in the rate determining step, as found for the reduction of quinones by ascorbic acid (Isaacs and Eldik 1997), which apparently leads finally to the increase in nanorod length.

As a consequence of these findings, this study is underlain by the idea that a diminution of the reaction rate by usage of a weaker reducing agent than ascorbic acid might also increase the aspect ratio of gold nanorods. Ascorbic acid is widely known as a reducing agent for

gold ions since it was shown already in 1937 (Brintzinger 1937) that the reduction of gold ions by ascorbic acid at room temperature leads to a red solution, characteristic for small gold particles as demonstrated in 1802 by Richter (Richter 1802). However, while the reduction of gold(III) by ascorbic acid at room temperature is very fast (Brintzinger 1937), remarkably, ascorbic acid is not capable of reducing Au^{III} to Au^0 in the presence of CTAB without small colloidal gold particles acting as seeds (Jana et al. 2001a).

In fact, dihydroxybenzenes and glucose might give rise to even slower reduction as the reduction potential decreases in the following order at a specific pH value: ascorbic acid, hydroquinone, catechol and resorcinol (Steenken and Neta 1982). Dihydroxybenzenes have already been used as reducing agents to prepare spherical particles (Henrich 1903; Garbowski 1903), where the resulting colour of the solution was dependent on the pH value: at a pH value below 7 green and blue and above pH 7 purple or red gold dispersions were obtained (Henrich 1903; Garbowski 1903). As the colour of gold dispersions is a certain indicator for the particle size, larger particles shift the colour towards blue (Mie 1908).

Accordingly, the aim of this study is to study the influence of weak reducing agents (and pH value) on the aspect ratio of gold nanorods.

Results

Gold nanorods (or nanowires, respectively) were prepared on the basis of a seed-mediated method and purified by a centrifugation procedure (details see experimental section). However, while ascorbic acid has been used so far as reducing agent in the growth solutions, milder reducing agents were employed under the same experimental conditions, namely dihydroxybenzenes and glucose. Experiments with temperature variations did not lead to a significant influence on the resulting products, while a decrease in CTAB concentration diminished nanorod formation.

Synthesis of gold nanorods with dihydroxybenzenes

Hydroquinone, catechol and resorcinol were employed, which are reducing agents of decreasing strength (Henrich 1903). The particle dispersions resulting from

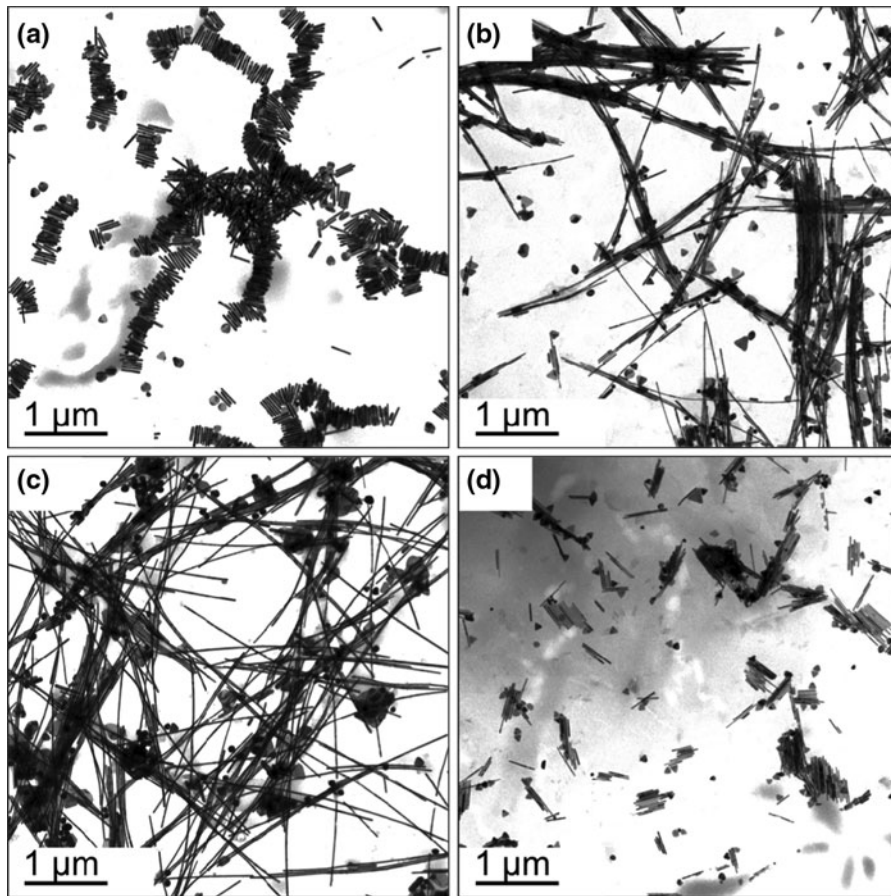


Fig. 1 TEM images of gold nanorods (or nanowires, respectively) prepared with different reducing agents. **a** ascorbic acid (pH value ≈ 3.7), **b** hydroquinone (pH value ≈ 4), **c** catechol (pH value ≈ 4), **d** resorcinol (pH value ≈ 4)

reduction of gold ions by hydroquinone or catechol showed an intense pinkish colour after 3 h, while dispersions prepared with resorcinol exhibited only a light pinkish colour after 192 h. These colour changes gave a first hint that resorcinol is indeed the weakest reducing agent as the low colour intensity of the final dispersions indicates a low concentration of nanoparticles. The following experiments refer to a reaction time of 24 h, where the reactions were apparently finished with the exception of that with resorcinol.

Statistically representative transmission electron microscopy (TEM) images illustrate the pronounced influence of the reducing agent to the aspect ratio of the gold particles. While the average width of gold nanoparticles was similar in all cases (~ 30 nm), the commonly applied reducing agent ascorbic acid led to nanorods with a length of 100–300 nm whereas hydroquinone and catechol induced formation of nanorods (nanowires) with exceptional lengths

(1–3 μm), i.e. an order of magnitude larger than that of the nanorods after 24 h of growth in presence of ascorbic acid, thus resulting in aspect ratios around 100 (Fig. 1a–c). Note that the scale bars in Fig. 1 are the same in each image, and, therefore, it becomes instantly evident that the difference between the nanorods prepared with the common reducing agent ascorbic acid on one hand and with hydroquinone or catechol on the other hand is enormous. A significant quantity of gold nanorods with a length between 300 and 900 nm also formed upon exposure of gold ions to resorcinol (Fig. 1d); however, the quantity of gold particles after 24 h was low compared to hydroquinone and catechol because of very low reduction rate.

Synthesis of gold nanorods with glucose

When glucose was applied as a reducing agent, again gold nanorods with very high aspect ratios arose, with

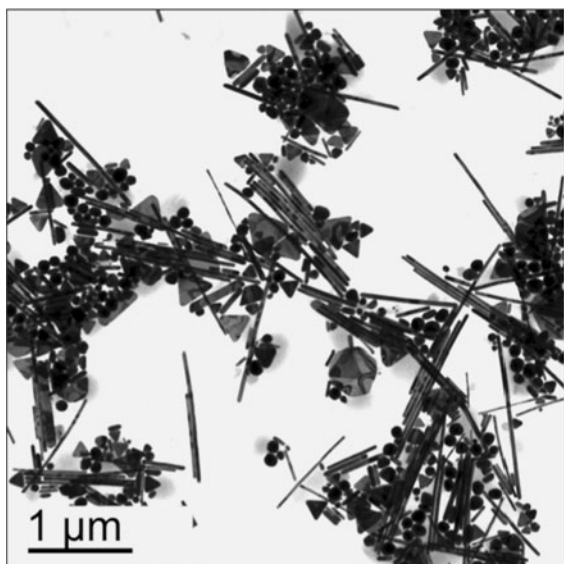


Fig. 2 TEM image of gold nanorods (or nanowires, respectively) prepared with glucose monohydrate (pH value ≈ 10.5)

lengths ranging from 1 to 2 μm (Fig. 2), when an optimum pH value of around 10.5 (see below) was adjusted with sodium hydroxide. Yet compared to the nanorods arising from reduction of gold ions with ascorbic acid or dihydroxybenzenes, the average width of anisotropic gold nanoparticles resulting from reduction with glucose (~ 40 nm) was slightly larger. Yet under the action of glucose also a significant quantity of particles with other shapes arose, such as triangles and platelets, which could not be separated with the employed technique described in the experimental section. The size of these particles seems to be increased compared to the particles with the same shapes emerging as side products when dihydroxybenzenes or ascorbic acid had been applied as reducing agent.

Dependence of nanorod formation on the pH value

An influence of the size of spherical gold particles by the pH value upon reduction of gold ions with dihydroxybenzenes or ascorbic acid is indicated by the different colours of the corresponding dispersions synthesized at pH values below 7 and above 7 (Brintzinger 1937; Henrich 1903; Garbowski 1903). Therefore, the influence of the pH value on the dimensions of gold nanorods was investigated in this study in the cases of ascorbic acid, hydroquinone and glucose. The initial growth solutions were acidic, mainly due to the starting material

tetrachloroauric acid (pH values about 3). In order to shift the values towards the alkaline region, sodium hydroxide was added, e.g. to yield final sodium concentrations of 5.49×10^{-4} M, 8.23×10^{-4} M, 1.1×10^{-3} M, 1.37×10^{-3} M, 1.65×10^{-3} M or 5.49×10^{-3} M. If ascorbic acid or hydroquinone was used as reducing agent, the quantity of high aspect ratio gold nanorods decreased with increasing pH value, and at pH values of 5–6 only few nanorods emerged anymore. In contrast, with glucose as reducing agent only spherical or particles with undefined shape arose at a pH value below 9, and an optimum performance of nanorods was found at a pH value of 10.5, i.e. at higher pH values (pH 11) the nanorod quantity decreased again.

Finally, it has to be mentioned that the synthesis with hydroquinone in the absence of NaOH has to be performed very carefully. A slight change in synthesis parameters (e.g. quality of water) can already lead to different results (undefined shapes) or even to the suppression of nanoparticle formation.

High resolution transmission electron microscopy (HRTEM) analysis of gold nanorods

In the presence of silver nitrate, the structure of the seed was reported to determine the structure of the finally resulting objects (Liu and Guyot-Sionnest 2005). Thus, single crystalline gold seeds grow into single crystalline nanorods while multiply twinned gold seeds grow predominantly into pentatwinned bipyramids (Liu and Guyot-Sionnest 2005). Gold nanorods which were prepared in the absence of silver nitrate were found to be penta-twinned along the growth direction, which is the [1 1 0] direction, without any further dislocations or stacking faults (Johnson et al. 2002). However, TEM investigations revealed a significant amount of bent nanowires. The bending of gold nanowires made a characterization of the crystallographic structure of those nanowires indispensable as defects could be responsible for this effect. Therefore, several HRTEM micrographs along one nanowire were recorded (Fig. 3–5). One end of a gold nanowire is presented in Fig. 3. The corresponding fast Fourier transform (FFT) patterns indicated the presence of twins along the growth direction, that is the [110] direction, due to the presence of three different zone axes. Along the nanowire, contrast changes were observed (Fig. 4). These changes could be a consequence of simple bending of the nanowire in the image plane or due to

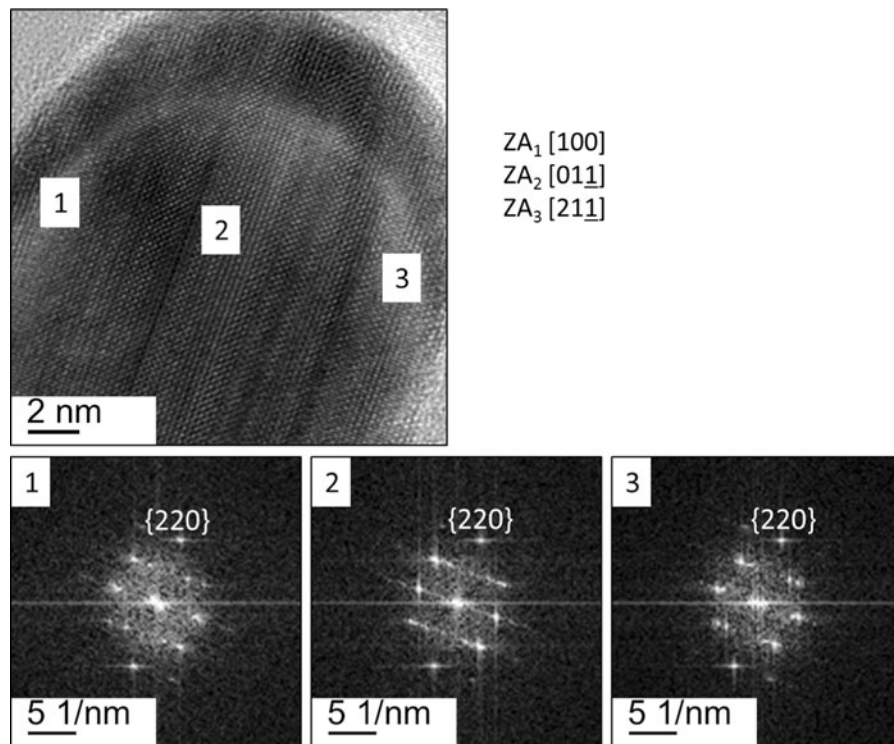


Fig. 3 HRTEM image of a gold nanowire and related FFT patterns (*marked spots*). Three different zone axes were determined indicating the presence of twins growing along the [110] direction

existing defects such as stacking faults or dislocations. FFT patterns of different spots around the dark contrast do not indicate any additional defects to the existing twins. The FFT pattern of spot 5 presents intensities which could not be indexed. In order to prove if defects are responsible for these non-identified intensities, additional experiments were performed. For these experiments the TEM holder was tilted first by 5° and finally by 10° , and HRTEM images were subsequently recorded at the same spot (Fig. 5). The neighbouring particles were used as identification mark to find the same spot (TEM micrographs). Remarkably, neither dislocations nor stacking faults could be found in $2 \mu\text{m}$ long nanowires. Thus, these nanowires also show only the penta-twinned structure along the growth direction.

Discussion

The aspect ratio of gold nanorods synthesized by a seed-mediated procedure could be enhanced drastically, i.e. by an order of magnitude, by application of weak reducing agents instead of the commonly applied

ascorbic acid. Notably, already in 1903 hydroquinone, catechol and resorcinol were used as reducing agent for the preparation of colloidal gold dispersions (Henrich 1903; Garbowski 1903), however, in the absence of a structure-directing agent such as CTAB. The obtained colour of those solutions was not only dependent on the reducing agent but also on the pH value of the reaction mixture. Green and blue solutions were obtained in the case of hydroquinone and catechol applied at a pH value below 7, and red or purple solutions at a pH value above 7 (Henrich 1903). Garbowski (1903) observed a slight difference in the colour of colloidal gold dispersions prepared with resorcinol, hydroquinone and catechol as reducing agents when comparing samples prepared at the same concentrations. Samples prepared with resorcinol showed less intense colour compared to the other samples. Also, an increase in reducing agent concentration led to an increase in colour intensity. A colour change to red or purple was obtained when neutralizing solutions with potassium carbonate (Garbowski 1903), again indicating that the pH value has an influence on particle growth. Thus, the above implication that the rate of the reduction of gold

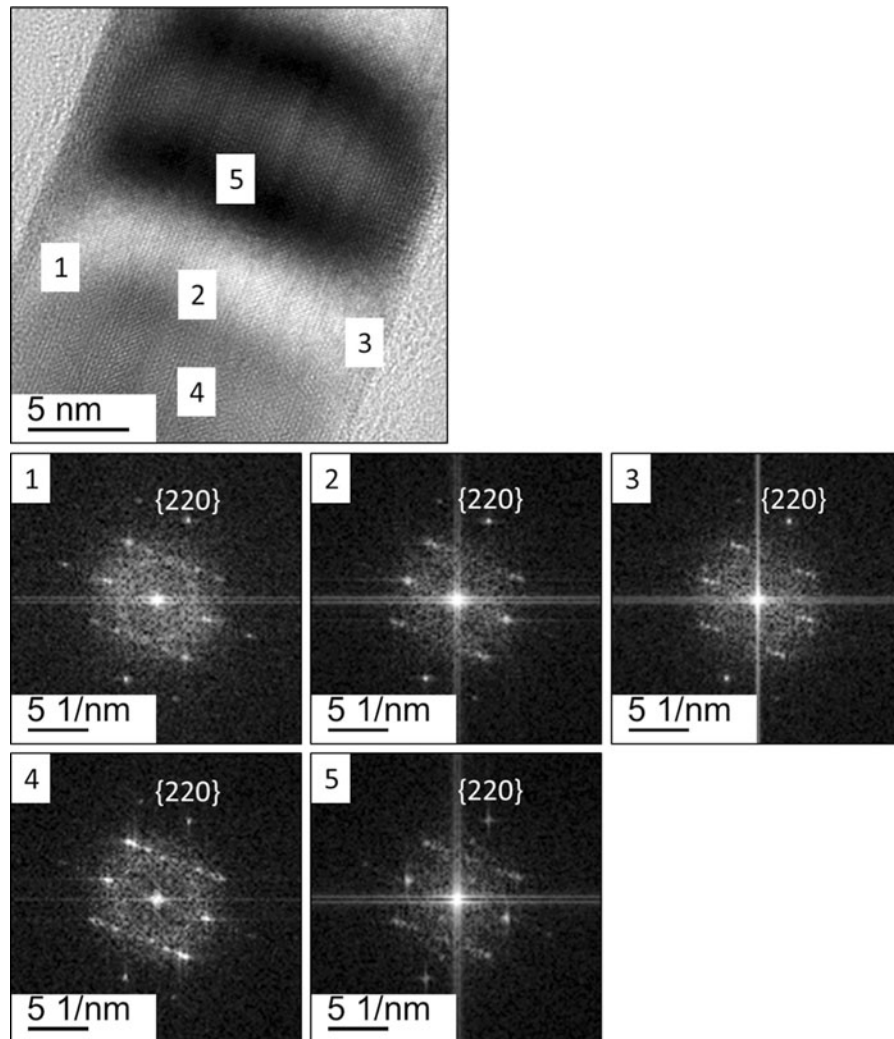


Fig. 4 HRTEM image of a gold nanowire presented in Fig. 4 at another spot of the wire and corresponding FFT patterns (*marked spots*). Here, a different contrast was observed. The growth direction still is the [110] direction

ions with resorcinol appears to be too slow for efficient nanoparticle generation is in line with the experiments of this study, where nanorod formation under the action of resorcinol was less expedient. Also, the above implied pH dependence of particle formation in the case of spherical particles is reflected in the seed-mediated growth method.

As mentioned above, the reduction potential of ascorbic acid, hydroquinone, catechol and resorcinol decreases in this sequence (Steenken and Neta 1982). Thus, the replacement of ascorbic acid by these dihydroxybenzenes leads to a decrease of the gold particle growth rate. In general, a decrease in the rate of chemical processes is often associated with higher

selectivity in product formation; i.e. anisotropic particle growth may be favored when the reaction slows down in the presence of a structure-directing agent (e.g. CTAB). Yet the process of nanorod formation is complex, and, therefore, the length of the rods does not increase simply with decreasing reduction potential of the reducing agent; for instance resorcinol is a weaker reducing agent than hydroquinone and catechol but the latter gave rise to particles with higher aspect ratios. Besides other effects such as coordination of the reducing agents to gold ions and surfaces of the (growing) particles, the reduction potential of the applied reducing agents changes with the pH value because H^+ is formed upon reduction of gold ions. At a pH

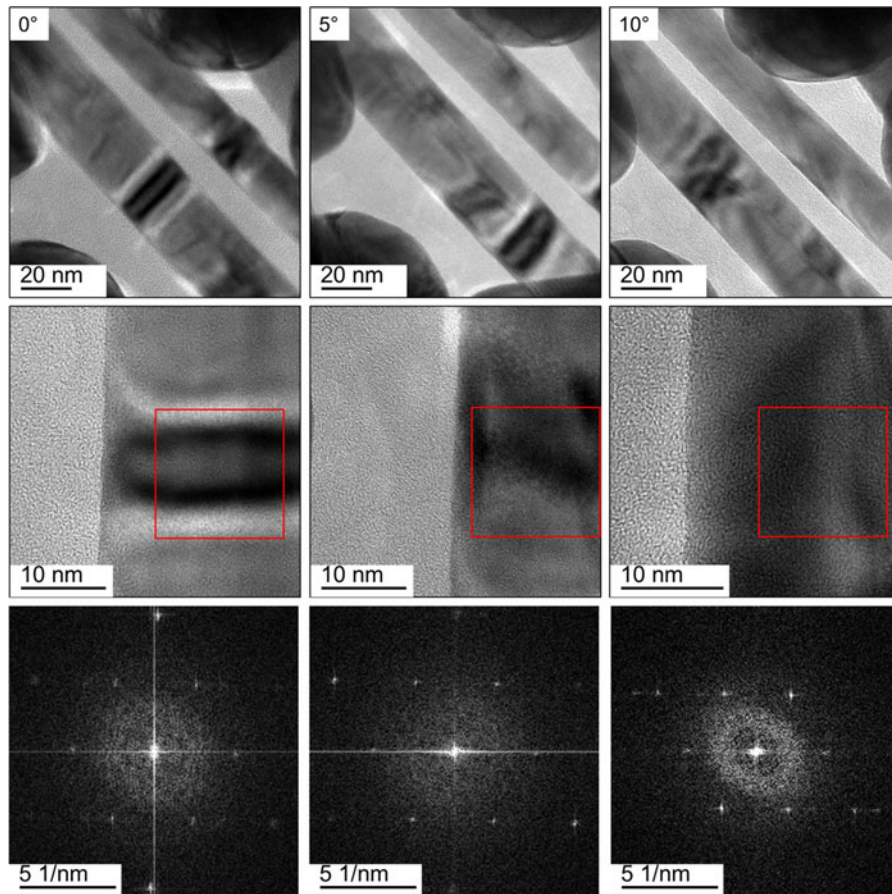


Fig. 5 *Topmost row from left to right: TEM images of a gold nanowire tilted by 0°, 5° and 10°, respectively. Medium row: HRTEM images corresponding to the TEM images in the*

value equal to the pK_a value of the reducing agent, half of the reducing agent is protonated. The pK_a value for ascorbic acid, hydroquinone and glucose has been reported to be 4.1, 9.91 and 12.28 in aqueous solution at 25 °C (Gokel 2004), which was confirmed by our own determinations in the presence of 0.1 M CTAB for ascorbic acid and hydroquinone (4.09 and 9.93, respectively). The maximum aspect ratio was found in each of these cases at a pH value below the pK_a value of the respective reducing agent. Therefore, it seems that a pH value below the pK_a value of the reducing agent is essential for the formation of gold nanowires. This is most likely due to the fact that the protonated reducing agents are weaker reducing agents (Pal et al. 1998), which makes the reduction slower and apparently more selective. However, if the reduction potential of the reducing agent is too low, the reducing agent is not capable of reducing the gold salt

topmost row. Lowermost row: FFT patterns corresponding to the images above. Particle growth proceeds in the [110] direction

expediently and nanoparticle formation is hampered, which seems to be the case for the resorcinol-mediated synthesis.

While nanorods prepared with ascorbic acid or hydroquinone had almost the same width, nanorods synthesized with glucose showed a larger width. This could be a consequence of differences in the surface charge of the growing gold particles due to the different pH values in the optimum range of nanorod generation with the respective reducing agents, which also could change the adsorption behaviour of the charged surfactant.

Careful investigations of the crystallographic structure of gold nanowires (tilting experiments) revealed that penta-twinned gold nanowires were present, which did not exhibit any further defects such as stacking faults and dislocations. This led to the conclusion that the same growth mechanism takes

Table 1 Estimated relative total areas of differently shaped gold particles in TEM images

Reducing agent	Shape	Before centrifugation (%)	After centrifugation (%)
Ascorbic acid	Rods	14	83
	Polyhedra	2	11
	Spheres	84	6
Hydroquinone	Rods	22	85
	Polyhedra	2	12
	Spheres	76	3
Catechol	Rods	32	86
	Polyhedra	6	8
	Spheres	62	6
Resorcinol	Rods	23	74
	Polyhedra	7	17
	Spheres	70	9
Glucose	Rods	50	52
	Polyhedra	21	26
	Spheres	29	22

In the case of glucose as the reducing agent, the particle sizes of the respective types of shape were very heterogeneous, thus particularly limiting the precision of the estimations

place as for penta-twinned gold nanorods described previously which bases on the preferred adsorption of CTAB onto the {100} side facets (Koepl et al. 2011; Johnson et al. 2002; Murphy et al. 2005).

In order to obtain an impression on the particle separation process by centrifugation (see experimental section, note that adsorption of CTAB obviously plays an essential role), the population of the differently shaped particles was estimated by evaluation of TEM images (Table 1). Except in the case of glucose as a reducing agent, which led to a very heterogeneous size distribution of the objects, centrifugation led mainly to removal of spheric particles, as also reported in samples with lower-aspect-ratio nanorods (Khanal and Zubarev 2008). Gold polyhedra (platelets) may further be removed from rods by an oxidation process, taking into account that this process is associated with a certain decrease in aspect ratio of the rods (Khanal and Zubarev 2008). As a side remark, in contrast to samples with relatively low gold aspect ratio, samples with high gold aspect ratios as present here can hardly be characterized by UV-vis spectroscopy because the absorption wavelength of the longitudinal surface plasmon band is above the range accessible in water or

deuterium oxide, and the transversal band is very weak and overlaps with the surface plasmon band of spheric particles (Koepl et al. 2012).

Conclusions

In seed-mediated processes for gold nanorod synthesis, simple replacement of the commonly applied ascorbic acid by dihydroxybenzenes or glucose results in a huge increase in aspect ratios up to an order of magnitude. Thus gold nanowires with aspect ratios around 100 and average lengths of 1–3 μm can be obtained. The increase in aspect ratio is mainly due to an increase in length and not in diameter. Apparently, the higher aspect ratios are a consequence of a decrease in reaction rate under the action of weaker reducing agents. As the reduction potential of the reducing agents strongly depends on the pH value, this quantity strikingly influenced the aspect ratios. It appears that the optimum pH value depends on the reducing agent and is below the pK_a value of the respective reducing agent. Best results were obtained with hydroquinone and catechol, whereas resorcinol seems to be too mild to reduce gold ions efficiently within 24 h, i.e. it appears that there is a certain optimum in strength of the reducing agent. The products consisted of penta-twinned gold nanowires without considerable defects such as stacking faults and dislocations. Most likely the generation of the nanorods proceeds by preferred adsorption of CTAB onto the {100} side facets of the gold particles.

Materials and methods

Materials

Hexadecyltrimethylammonium bromide (CTAB, $\geq 98\%$) was purchased from Sigma, hydrogen tetrachloroaurate trihydrate ($\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$, 99.99%) from Johnson Matthey, sodium citrate dihydrate (99%) from Sigma, sodium borohydride (NaBH_4) from Fisher Scientific (general purpose grade), L-ascorbic acid and glucose monohydrate from Hanseler AG (Herisau, Switzerland), hydroquinone from Sigma ($>99\%$), catechol from ABCR-Chemicals (99%, Karlsruhe, Germany) and resorcinol from Chemie Brunschwig AG (98%, Basel, Switzerland).

Sodium hydroxide was purchased in Titrisol® 0.1 M ampoules. For the preparation of all samples, freshly deionized H₂O was employed.

Synthesis of gold nanorods (or nanowires, respectively)

Recently, we reported a modified seed-mediated growth procedure, which was the basis for the synthesis of gold nanorods and nanowires in this study (Koepl et al. 2011). However, besides ascorbic acid, also hydroquinone, catechol, resorcinol or glucose were applied as reducing agents in the growth solution. Even though important experimental details described in literature (Koepl et al. 2011) should be considered, a short summary of a typical experiment is given in the following.

In a first step, 100 mL of a growth solution containing 0.1 M CTAB and 2.5×10^{-4} M H[AuCl₄] \cdot 3H₂O were prepared. This solution was kept at 33 °C for 24 h to completely dissolve the CTAB powder. Further, 20 mL of a seed solution containing small gold particles was prepared. The formation of these gold particles is based on the fast reduction of H[AuCl₄] \cdot 3H₂O by NaBH₄ in the presence of a stabilizing agent, here sodium citrate. This solution was kept undisturbed for 24 h at room temperature. During that time the seeds grew to ~8 nm diameter.

After 24 h, 80 µL of a freshly prepared 0.1 M reducing agent solution (8.0×10^{-6} mol reducing agent) were added to 14.4 mL of the growth solution (containing 3.6×10^{-6} mol gold). The solution was mixed by shaking, whereupon it became colourless in the case of ascorbic acid (indication for the reduction of Au^{III} to Au^I) and brighter yellow in the case of hydroquinone. The colour of the solution did not change for the other three used reducing agents. The addition of 16 µL of the seed solution (aged 24 h, containing 4.0×10^{-9} mol gold) and subsequent mixing of the solution by shaking led to a reddish colour of the solution. In some experiments, sodium hydroxide solution (e.g. 80 µL, 0.1 M, leading to a final pH around 4) was used to modify the pH value, added to the growth solution just before the addition of seed solution. In this case, after addition of the seed solution the reaction mixture became transparent for all reducing agents after a certain time (if not already transparent before addition of the seed solution). In particular, for resorcinol and glucose the colour

change was observed only after hours. Finally the test tubes were placed in a water bath at 33 °C for 24 h.

Shape separation of gold nanorods (or nanowires, respectively) from spherical gold nanoparticles

For the separation of gold nanorods and nanowires from spherical gold nanoparticles a centrifugation process was employed. Before the separation process was applied, a considerable part of the excess of CTAB had to be removed. For this purpose the samples were stored in a refrigerator for at least 24 h to precipitate a significant amount of CTAB before the cold dispersions were rapidly filtered through a sintered glass funnel. Afterwards, 1.5 mL of filtrate was centrifuged at 5,600 rpm for 20 min to concentrate the particles, using a Ministar centrifuge (VWR International, Dietikon, Switzerland). The transparent supernatant was discarded by decantation and the nanoparticles, which assembled at the bottom of the centrifugation tube were collected and redispersed in 1.5 mL of a 0.1 M CTAB solution. This solution was kept undisturbed for 2 h. After this time, the sample was centrifuged again at 5,600 rpm for 1 min. The pinkish supernatant, containing mostly spherical particles and excess CTAB, was discarded and the redispersion and centrifugation process was repeated once more. The particles, which were collected at the bottom of the centrifugation tube as well as partly on the wall of the tube, were finally redispersed in 0.5 mL deionized water. Afterwards, the solution was sonicated for 90 min to get a well-dispersed solution, to remove the attached particles from the centrifugation tube wall and to avoid agglomeration.

Transmission electron microscopy

For investigation with transmission electron microscopy (TEM) a Philips CM200 (160 kV acceleration voltage) and for high resolution transmission electron microscopy (HRTEM) a Technai F30 (300 kV accelerating voltage) was used. The average length, width and aspect ratio of the nanorods were determined by counting several hundred particles with an aspect ratio greater than two (manual evaluation of several TEM images). Since the gold nanowires are mostly bent on the TEM grid, only an end-to-end measurement of the length of the nanowires was possible, which may lead to a certain deviation in the measurement of the

average values for the aspect ratio and the length of the nanowires. Therefore, a range is given for the length of gold nanowires. In order to obtain reliable images, one droplet ($\approx 0.5 \mu\text{L}$) of the filtered and shape separated solution was placed on a commercially available carbon-coated copper TEM grid (Plano GmbH, Wetzlar, Germany).

Acknowledgments We cordially thank Stephan Frank (MAT LAB routine for size evaluation) and Martin Süess (HRTEM) for technical assistance, Irene Bräunlich for fruitful discussions, the electron microscopy center (EMEZ) of ETH Zurich for support and the Swiss National Science Foundation (SNSF) for financial support under Project no. 200021-113463.

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