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Kinetically controlled growth of gold nanotriangles in a vesicular template phase by adding a strongly alternating polyampholyte

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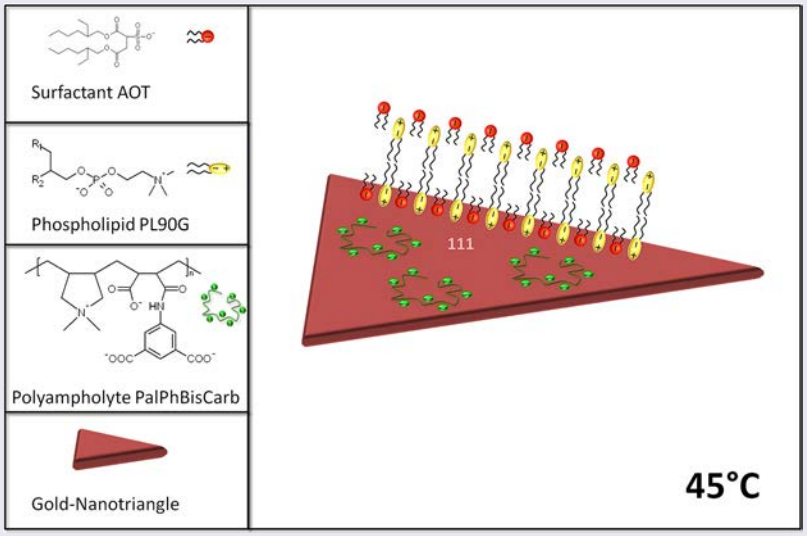
ABSTRACT

This paper is focused on the temperature-dependent synthesis of gold nanotriangles in a vesicular template phase, containing phosphatidylcholine and AOT, by adding the strongly alternating polyampholyte PalPhBisCarb.

UV-vis absorption spectra in combination with TEM micrographs show that flat gold nanoplatelets are formed predominantly in the presence of the polyampholyte at 45°C. The formation of triangular and hexagonal nanoplatelets can be directly influenced by the kinetic approach, i.e., by varying the polyampholyte dosage rate at 45°C. Corresponding zeta potential measurements indicate that a temperature-dependent adsorption of the polyampholyte on the {111} faces will induce the symmetry breaking effect, which is responsible for the kinetically controlled hindered vertical and preferred lateral growth of the nanoplatelets.

GRAPHICAL ABSTRACT



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Kinetically controlled nanocrystal growth; nanotriangles; polyampholytes

Introduction

Size and shape control of gold nanoparticles has been the focus of a lot of investigations due to the size- and shape-dependent physicochemical and optical properties, which are of special interest in different fields of application, e.g., in photonics, catalysis, and biomedicine.[1]

Spherical gold nanoparticles are well known over a long time period, starting from the experiments of the alchemists in the 16th century up to now. The mechanism of the gold nanoparticle formation via a nucleation process is well established, and the size of the spheres can be varied in a broad range from 2 up to 200 nm. Turkevich et al. produced gold nanoparticles of small dimensions by using citric acid as a reducing agent in a highly diluted aqueous solution.[2] This process was refined by Frens for the synthesis of citrate stabilized gold nanoparticles, the most commonly employed aqueous method to control the size and size distribution of the gold nanoparticles by the reaction conditions.[3] However, the stability of gold nanoparticles stabilized by citric acid is limited and ultra-small

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monodisperse particles with particle dimensions <2 nm can only be prepared by reducing the gold chloride solution with $NaBH_4$ according to the procedure developed by Brust et al.[4]

The resulting monodisperse very small gold nanoparticles can be used as seeds. A seeding growth preparation of spherical nanoparticles of 5–40 nm diameter can be performed, as shown by Jana et al.[5] Bastus et al. discussed a kinetically controlled seeded growth synthesis of citrate-stabilized nanoparticles up to 200 nm, according to an Ostwald ripening in the second period of the LaMer mechanism.[6]

Furthermore, the seed-mediated synthesis can be used for making gold nanoparticles of different shapes. The surfactant assistant approach, using the cationic surfactant CTAB, leads to the formation of gold nanocrystal seeds of about 1.5 nm, which grow up in the following step to anisotropic nanorods or flat nanoplatelets.[7]

In the shape-controlled synthesis, thermodynamic or kinetic-controlled processes play an important role. From the energetic point of view spherical particles should be formed, which means for the formation of anisotropic particles a higher activation energy is required.[8]

The formation of energetically unfavorable anisotropic nanorods or nanoplatelets can be forced:

1. By adding symmetry breaking components

Polymers, like poly(vinyl pyrrolidone) (PVP),[9] surfactants, e.g., CTAB,[7,10] as well as ions, e.g., iodide,[11–13] can overcome the role of a directing agent for anisotropic growth as blocking species on certain {111} crystal facets of the gold nanoparticles. The leaf extract of lemongrass can have a similar effect.[14]

2. By using template phases

directing the anisotropic growth in one direction. Micellar templates can do that in a characteristic way.[15]

However, the other general way to come to anisotropic nanocrystals is a kinetic approach. In that case anisotropic gold nanoparticles are formed at slow rates of reaction by adding mild reducing agents. Therefore, the growth can be directed in lateral direction and flat nanoplates or truncated bitetrahedra are formed.[8,11]

The kinetically controlled growth of the nanoparticles opens a way to come to anisotropic gold crystallites, i.e., rods, cubes, discs, cages, pyramids, or triangles.[7,16,17] In our previous work, we were able to show that triangular gold nanoplatelets are formed in a vesicular template phase in the presence of a strongly alternating polyampholyte, i.e., poly(*N,N′*-diallyl-*N,N′*-dimethylammonium-alt-3,5-bis(carboxyphenyl)maleamic carboxylate (PalPhBisCarb).[18,19] Unfortunately, the role of the polyampholyte PalPhBisCarb is not really understood in this procedure. On the one hand, we know that the polymer can transform a mixed dioctyl sodium sulfosuccinate (AOT) vesicle phase into a tubular network structure[20] and on the other hand it can increase the amount of nanotriangles.[18,19] Recently, we have shown that the process of gold nanotriangle formation at room temperature can be described by an Ostwald ripening growth mechanism (not yet published). In the present work we want to study the role of the polyampholyte in more detail, especially with regard to the kinetically controlled growth of the nanocrystals by adding the polyampholyte at various dosage rates. The aim of the study is to understand the symmetry braking effect of PalPhBisCarb in relation to the Lofton/Sigmund model of a growth in lateral direction.[21]

Experimental

Materials

The alternating copolymer poly(N,N′-diallyl-N,N′-dimethylammonium-alt-3,5-bis-carboxyphenyl-maleamic carboxylate (PalPhBisCarb) with a molecular weight of about 15,000 g/mol was synthesized by free radical polymerization, shown by us earlier.[22]

The phospholipid PL90 G (>97.3%, 1.5% lysophosphatidylcholine) was obtained from Phospholipid GmbH. The anionic surfactant dioctyl sodium sulfosuccinate AOT (>98%) purchased from Sigma-Aldrich was used as given. The hydrogen tetrachloroaurate $HAuCl_4$ was purchased from Aldrich, and water was used after purification with the Milli-Q Reference A + system from Millipore.

Vesicle template phase formation

The vesicle phase was produced by dissolving a PL90G–AOT mixture (1:1) in water under stirring for two days at room temperature in the absence and presence of PalPhBisCarb. The turbid dispersion was clarified in a sizing step by sonification for 5 minutes with an ultrasound finger.

Gold precursor solution

A 2 mM aqueous tetrachloroaurate solution was freshly prepared.

Gold nanoparticle formation

- Reference system

The mixed template/precursor solution in the absence and presence of PalPhBisCarb was used as a reference system to investigate the gold nanoparticle formation at different temperatures.

- Kinetic procedure 1

The vesicular template phase in the presence of PalPhBisCarb was used as a stock solution and the aqueous gold precursor solution was added stepwise at different temperatures.

- Kinetic procedure 2

The gold precursor solution was used as a stock solution and the vesicular template phase in the presence of PalPhBisCarb was added stepwise at different temperatures.

- Kinetic procedure 3

The aqueous PalPhBisCarb solution was added stepwise to the mixed template/precursor solution at different temperatures.

Methods

UV-vis experiments were performed with a Cary 500 (Fa. Varian) UV–vis–NIR spectrometer in the wavelength range between 400 and 1200 nm using quartz cuvettes with a path length of 1 cm.

The morphology and size of the gold particles was characterized by transmission electron microscopy. Gold nanoparticle dispersions were dropped on carbon-coated copper

grids and examined in the transmission electron microscope JEM-1011 (JEOL) at an acceleration voltage of 80 kV after solvent evaporation.

Dynamic light scattering (DLS) measurements were carried out at 25°C at a fixed angle of 173° using the Nano Zetasizer 3600 (Malvern), equipped with a He–Ne laser (4 mW) and a digital autocorrelator. To characterize the particle size distribution of the gold nanoparticles a multimodal peak analysis by intensity and number plot was used. The zeta potential of the particles was determined by using the Malvern Nano Zetasizer 3600.

Results

Color effects, UV-vis-NIR spectroscopy, and DLS results

Reference system in the absence of PalPhBisCarb

The DLS intensity plot of the template phase shows a bimodal particle distribution with one large peak at about 100 nm and a second one at about 30 nm (not shown here).

At room temperature (25°C) the optically clear solution starts to become red after 65 minutes. At the same time the UV-vis spectra show an absorption peak at about 520 nm, characteristic for the Plasmon resonance effect. This peak is increased in the next half hour drastically, indicating that spherical gold nanoparticles are formed.

When the same experiment is performed at 45°C, the gold nanoparticle formation starts after 20 minutes, as to be seen by a red color and the UV absorption at 520 nm. After 25 minutes a second absorption is observed between 700 and 1000 nm, characteristic for anisotropic gold nanoparticles.

Generally speaking, the gold nanotriangle formation process becomes much faster at higher temperatures, and the nucleation time can be reduced from 120 to 30 minutes by heating up the system to 45°C.

Reference system in the presence of PalPhBisCarb

In the presence of the polyampholyte in the template phase one can observe at room temperature (25°C) a second UV absorption maximum at 700 nm after 120 minutes (Figure 1). By increasing the reaction temperature to 45°C the nucleation process is reduced to 30 minutes, and the absorption peak for the anisotropic particles is increased significantly (Figure 1). The red color of the solution and DLS data underline these results. The number plot, detecting exclusively smaller particles, shows that at room temperature in the third part of the nucleation time period (after 90 minutes) larger particles are formed in contrast to the experiments performed at 45°C, where smaller particles become dominant in the corresponding time period (after 20 minutes) (Figure 2).

Kinetic procedure 1

When the PalPhBisCarb-containing template solution is added stepwise to the gold chloride precursor solution the temperature plays an important role, too. At room temperature the Plasmon resonance peak at 520 nm, corresponding to a small spherical gold nanoparticle fraction, is dominant. A second small peak between 750 and 800 nm indicates the formation of anisotropic particles (compare Figure 3). This peak is only marginally shifted by increasing the dosage rate.

At 45°C and low dosage rate the asymmetric peak at 748 nm becomes dominant. With increasing dosage rate a significant stepwise shift to 792 and 928 is observed. DLS data show the same trend which means a shift of the number peak from 10 to 20 nm. These data clearly show that asymmetric gold nanoparticles of larger dimensions are predominantly formed at 45°C at higher dosage rates. Noteworthy that these findings are quite opposite to the seed-mediated synthesis of nanoplatelets in the presence of CTAB, where the best results were found at the lowest addition rate.[8]

A furthermore temperature increase to 70°C induces the opposite effect (Figure 3). This means the second absorption maximum is shifted to lower values, becomes less pronounced, and is decreased from 699 to 645 nm by increasing the dosage rate.

Kinetic procedure 2

When the template phase is used as the stock solution and the gold chloride solution is added stepwise with increasing dosage rate one can observe at room temperature a red shift of the second absorption peak from 852 to 729 nm (Figure 4).

At 45°C a significant shift with increasing dosage rate from 841 to 909 and finally 1010 nm can be observed. This effect is quite similar to the results discussed above (procedure 1) indicating the formation of larger nanotriangles at higher dosage rate.

At 70°C the asymmetric peak disappears completely (compare Figure 4), without any effect of the dosage rate.

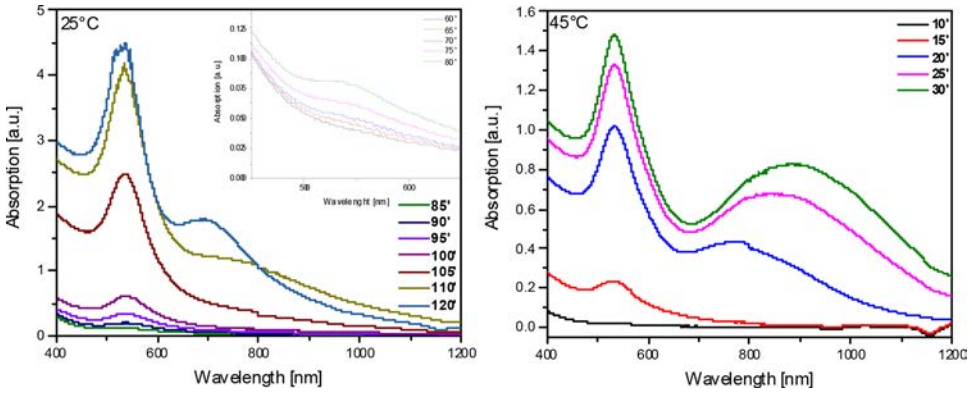

Figure 1. Time-dependent UV-vis absorption spectra of the reference system in the presence of PalPhBisCarb at room temperature and 45°C.

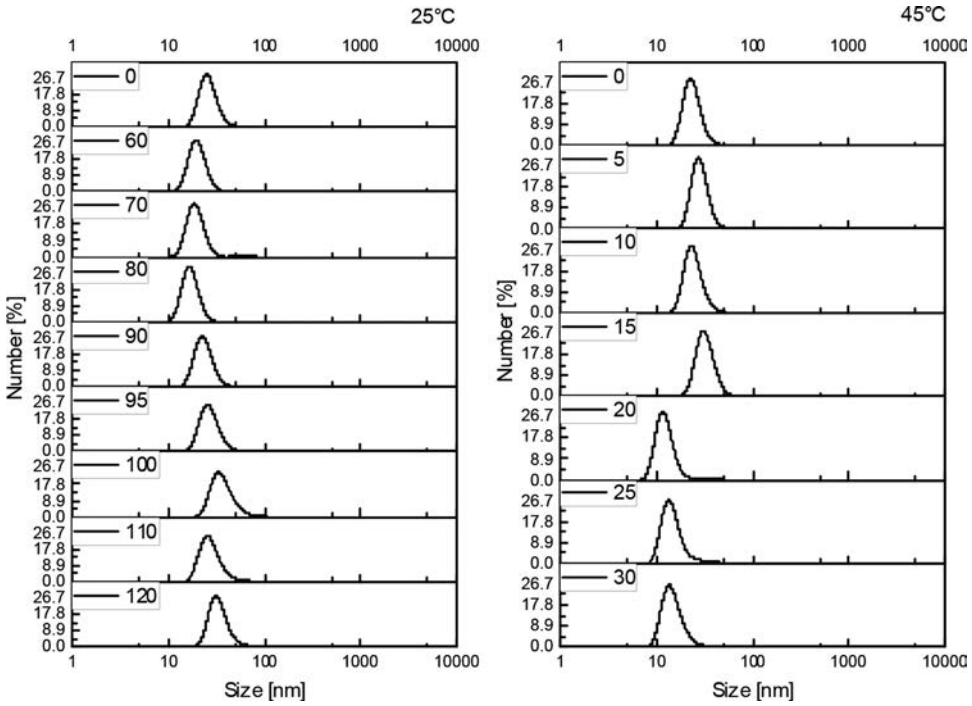

Figure 2. Time-dependent number plot of DLS spectra of the reference system in the presence of PalPhBisCarb at room temperature and 45°C.

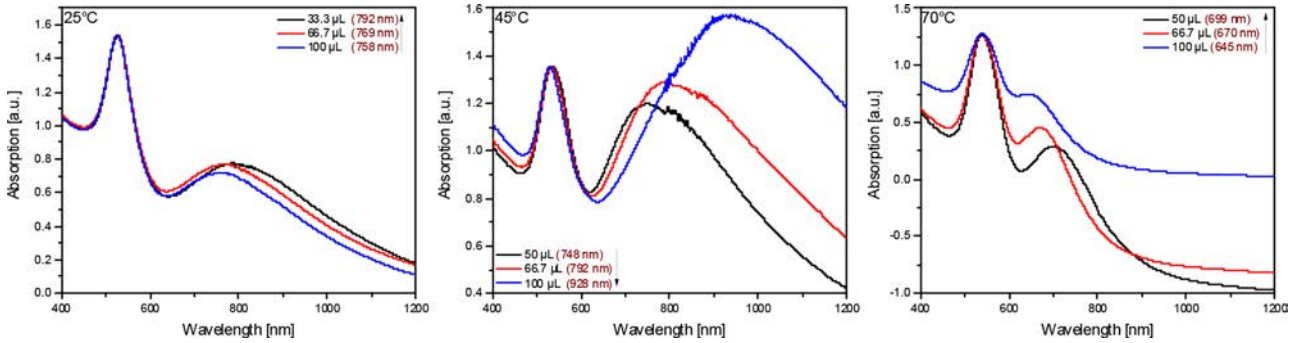

Figure 3. UV-vis absorption spectra according to the Kinetic Procedure 1 at room temperature, 45°C, and 70°C by varying the dosage rate.

Kinetic procedure 3

By mixing the template phase and the gold precursor solution at room temperature and adding the polyampholyte at room temperature or 45°C by varying the dosage rate, no effect was observed. That means under such conditions only spherical gold nanoparticles are formed but not yet anisotropic ones.

When the initial mixing temperature is 45°C one can see a different picture (Figure 5). By adding PalPhBisCarb at room temperature to the mixture a peak at 792 nm indicates the

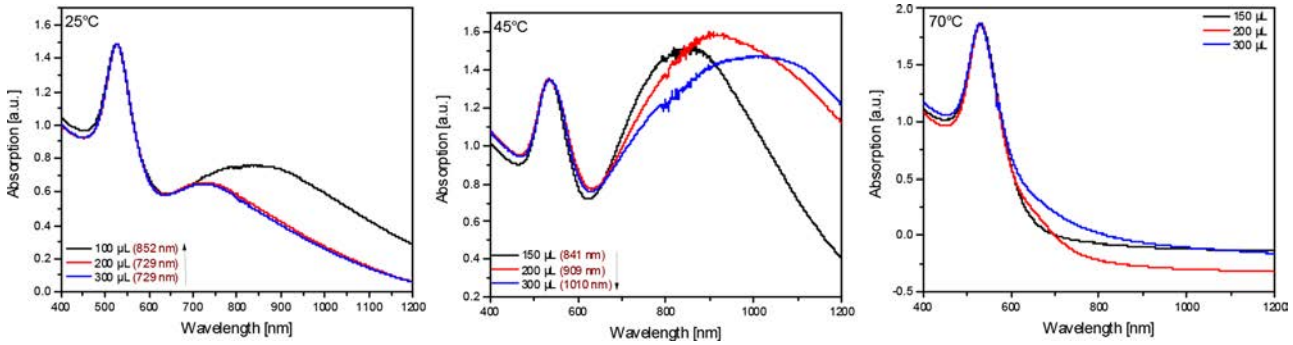

Figure 4. UV-vis absorption spectra according to Kinetic Procedure 2 at room temperature, 45°C, and 70°C by varying the dosage rate.

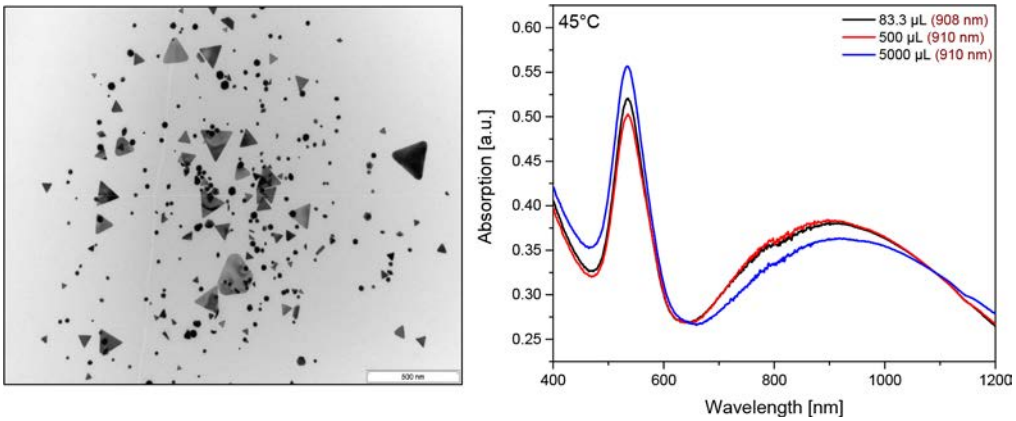

Figure 5. UV-vis absorption spectra of a precursor solution heated to 45°C by adding PalPhBisCarb at 45°C by varying the dosage rate with the corresponding TEM micrograph.

Table 1. Yield of anisotropic particles and triangles in dependence on the procedure, temperature, and dosage range.

Procedure	Temperature (°C)	Dosage rate (µL)	Anisotropic particles (in %)	Triangles (in %)
1	25	–	22 ± 1	9 ± 1
1	45	50	43 ± 2	22 ± 2
1	45	100	45 ± 1	23 ± 1
1	70	–	52 ± 2	18 ± 1
2	25	–	33 ± 1	10 ± 1
2	45	50	53 ± 3	28 ± 2
2	45	100	58 ± 4	29 ± 2
2	70	–	34 ± 2	6 ± 2

formation of asymmetric nanoparticles. When the polyampholyte addition is performed at 45°C the peak at 910 nm is enhanced (Figure 5). However, a clear influence of the dosage rate cannot be observed.

TEM characterization

For a more comprehensive characterization of the asymmetric nanoparticles, transmission electron microscopy (TEM) investigations were performed. Figure 5 shows for example the gold nanoparticles formed according to the Kinetic Procedure 3 at 45°C. One can see that in addition to spherical particles nanotriangles of different sizes are formed. Noteworthy, that the triangles are stable for a longer time without truncation of the triangle tips.

To compare the different samples the percentage of anisotropic nanoparticles and nanotriangles was determined (compare Table 1) and the triangle length was checked, as to be seen in Figure 6.

The highest yield of triangles is obtained by using the Kinetic Procedure 2, when the template phase with PalPhBisCarb is used as a stock solution and the gold chloride precursor is fast added at 45°C (Table 1). The same trend can be

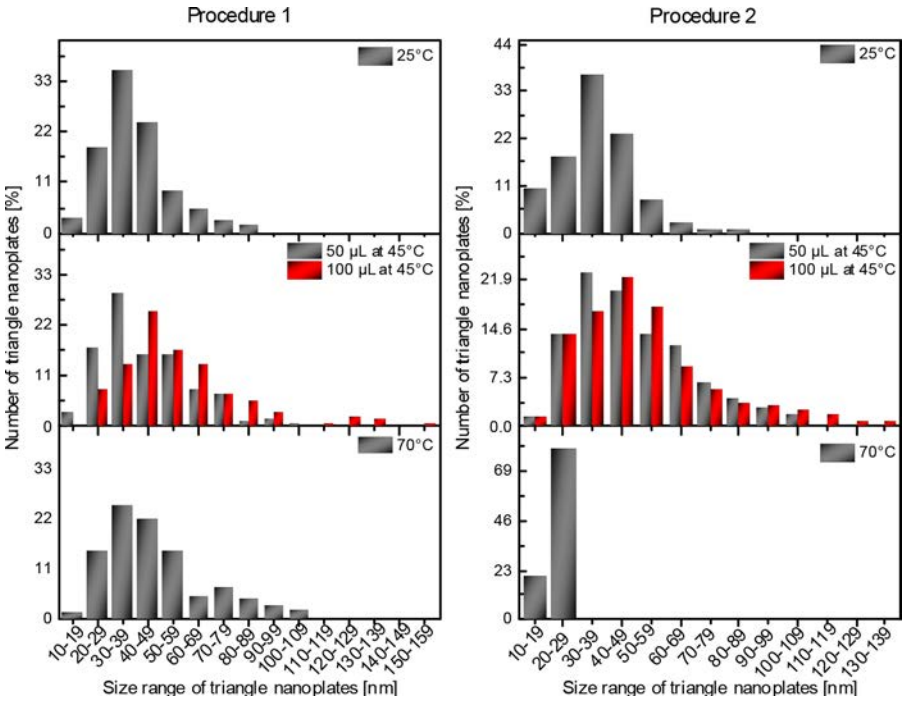

Figure 6. Edge length of anisotropic particles obtained by Kinetic Procedures 1 and 2 in dependence on temperature and dosage rate.

observed by using Procedure 1. Figure 6 documents that the edge length of the triangles is increased at faster dosage rate.

Discussion

Our experiments first of all show that nanotriangles are formed in the vesicular template phase in the absence of the polyampholyte only at higher temperatures, i.e., at 45°C. This is already a first hint that energetically non-preferred platelet structures are formed predominantly at higher temperatures due to the required higher activation energy, in comparison to spherical particles. In the presence of PalPhBisCarb the formation of triangles can be initiated at room temperature and is enhanced at 45°C. This shows the extraordinary effect of the polyampholyte. When the gold precursor is titrated with the template phase in the presence of PalPhBisCarb at 45°C the formation of nanotriangles can furthermore be controlled by the dosage rate of the vesicular template phase. In the opposite case, by adding the gold chloride solution to the template phase at 45°C a similar kinetically controlled process of nanotriangle formation takes place. Under these conditions the highest yield of nanotriangles (29%) with an edge length of about 45 nm is observed. The extraordinary effect of PalPhBisCarb is shown by adding the polyampholyte in a separate step, too. In that case the temperature effect is of dominance but not yet the kinetic effect of the dosage rate.

Separately performed zeta potential measurements show that the initial zeta potential of the template phase of -94 ± 4 mV is decreased by adding PalPhBisCarb to -68 ± 4 mV. This can be explained by a replacement of AOT by the polyampholyte PalPhBisCarb leading to mixed vesicles.

After the gold nanoparticle formation a similar zeta potential can be determined at room temperature. The experiments by adding the polyampholyte in an additional step (kinetic procedure 3) show a concentration-dependent decrease of the zeta potential to -79 ± 3 mV and -69 ± 3 mV by increasing the PalPhBisCarb concentration. This effect can be explained by the adsorption of the polyampholyte (with three carboxylic groups and one quaternary N function) on the surface of the gold nanoparticles and a replacement of the negatively charged AOT molecules with the strong acid sulfonate groups. Looking now to the zeta potential values at different temperatures (Kinetic Procedure 1), one can see an interesting trend.

When the experiments were performed at room temperature the final zeta potential will be in the same order as the template phase, this means -93 ± 4 mV. By increasing the reaction temperature to 45°C the zeta potential is decreased to -85 ± 4 mV. A furthermore increase to 70°C leads to an opposite effect and negative zeta potential is increased again.

This means at 45°C we observe a preferred adsorption of the PalPhBisCarb on the gold nanoparticle surface, in contrast to 70°C and room temperature.

Conclusions

Our temperature-dependent experiments show that the energetically non-preferred gold nanotriangles are predominantly formed at higher temperatures, i.e., at 45°C, because of the higher activation energy for the formation of anisotropic nanoparticles in comparison to the activation energy for isotropic ones.

Furthermore our experiments show the extraordinary effect of the polyampholyte PalPhBisCarb in dependence on temperature. That means at 45°C the adsorption of the polyampholyte on the {111} facets of the nanoplatelets is preferred leading to a lower zeta potential. At higher temperatures polyampholyte adsorption failed, and the yield of nanoplatelets is decreased.

Kinetic experiments performed at 45°C show that the yield and size of nanotriangles can furthermore be increased by increasing the dosage range. This means under fast reaction conditions more polyampholytes can adsorb on the {111} facets of gold platelets directing the crystallization in lateral direction and hindering the vertical growth according to the crystallization growth model developed by Lofton and Sigmund.[21]

References

[1] Daniel, M.-C. and Astruc, D. (2003) *Chem. Rev.*, 104: 293–346.
[2] Turkevich, J., Stevenson, P.C. and Hillier, J. (1951) *Discuss. Faraday Soc.*, 11: 55–75.
[3] Frens, G. (1973) *Nature*, 241: 20–22.
[4] Brust, M., Walker, M., Bethell, D., Schiffrin, D.J., and Whyman, R. (1994) *Chem. Commun.*, 7: 801–802.
[5] Jana, N.R., Gearheart, L., and Murphy, C.J. (2001) *Langmuir*, 17: 6782–6786.
[6] Bastus, N.G., Comenge, J., and Puntes, V. (2011) *Langmuir*, 27: 11098–11105.
[7] Smith, D.J. and Korgel, B.A. (2008) *Langmuir*, 24: 644–649.
[8] Hong, S., Acapulco, J.A.I., Jang, H.-J., Kulkarni, A.S., and Park, S. (2014) *Bull. Korean Chem. Soc.*, 35: 1737–1744.
[9] Seo, D. and Song, H.J. (2009) *Am. Chem. Soc.*, 131: 18210–18211.
[10] Scarabelli, L., Coronado-Puchau, M., Giner-Casares, J.J., Langer, J., and Liz-Marzan, L.M. (2014) *ACS NANO*, 6: 5833–5842.
[11] Lohse, S.E., Burrows, N.D., Scarabelli, L., Liz-Marzan, L.M., and Murphy, C.J. (2014) *Chem. Mat.*, 26: 34–43.
[12] Rai, A., Singh, A., Ahmad, A., and Sastry, M. (2006) *Langmuir*, 22: 736–741.
[13] Kim, J., Hong, S., Jang, H.-J., Choi, Y., and Park, S. (2013) *J. Colloid Interf. Sci.*, 389: 71–76.
[14] Shankar, S.S., Rai, A., Ahmad, A., and Sastry, M. (2005) *Chem. Mater.*, 17: 566–572.
[15] Ding, W., Lin, J., Yao, K., Mays, J.W., Ramanathan, M., and Hong, K. (2013) *J. Mat. Chem. B*, 1: 4212–4216.
[16] Skrabalak, S.E., Chen, J., Sun, Y., Lu, X., Au, L., Cobley, C. and Xia, Y. (2008) *Acc. Chem. Res.*, 41: 1587–1597.
[17] Lee, J., Hasan, W., Stender, C.L., and Odom, T.W. (2008) *Acc. Chem. Res.*, 41: 1762–1771.
[18] Schulze, N., Prietzel, C., and Koetz, J. (2016) *Coll. Polym. Sci.*, 294: 1297–1304.
[19] Liebig, F., Sarhan, R.M., Prietzel, C., Reinecke, A., and Koetz, J. (2016) *RSC Adv.*, 6: 33561–33568.
[20] Schulze, N., Appelhans, D., Tiersch, B., and Koetz, J. (2014) *Colloids Surf. A*, 457: 326–332.
[21] Lofton, C. and Sigmund, W. (2005) *Adv. Funct. Mater.*, 15: 1197–1208.
[22] Fechner, M. and Koetz, J. (2011) *Macromol. Chem. Phys.*, 212: 2691–2699.