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Thermal stability of mesoporous silica-coated gold nanorods with different aspect ratios

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HIGHLIGHTS

- Deformation of mesoporous silica-coated gold nanorods upon annealing up to 900 °C.
- The silica shell protects the gold cores from turning into spheres up to 500 °C.
- Decreasing thermal stability with increasing aspect ratio.
- Deformation of the silica shell dictated by the shape change of the gold core.
- Core induced break-up of the shell for high aspect ratio nanorods.

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ABSTRACT

The effect of different temperatures (up to 900 °C) on the morphology of mesoporous silica-coated gold nanorods was systematically investigated. Gold nanorods with different aspect ratios (AR ranging from 2.5 to 4.3) were coated with a 15 nm thick mesoporous silica shell. Silicon supported monolayers of the particles were annealed in the temperature range of 300–900 °C. The resulting changes in particle morphology were investigated using scanning electron microscopy and visible wavelength extinction spectroscopy. The silica coating generally improved the stability of the nanorods from ca. 250 °C by several hundreds degree Celsius. For nanorods with AR < 3 the shape and the aspect ratio change is only moderate up to 700 °C. At 900 °C these nanorods became spherical. For nanorods with AR>3, lower stability was found as the aspect ratio decrease was more significant and they transformed into spherical particles already at 700 °C. It was confirmed by investigating empty silica shells that the observed conformal change of the shell material when annealing core/shell particles is dictated by the deformation of the core particle. This also implies that a significant mechanical stress is exerted on the shell upon core deformation. In accordance with this, for the highest aspect ratio (AR ~ 4) nanorod the shell breaks up at 900 °C and the gold cores were partially released and coalesced into large spherical particles.

1. Introduction

Due to the special optical properties of noble metal nanoparticles, they have been studied very intensively in the last decades. The plasmonic properties of gold nanorods allow them to be used in photothermal therapy [1,2], imaging techniques [3,4], theranostics [5,6], sensing applications [7–10] and optical memories [11,12].

The shape deformation and melting point decrease of nanoparticles was observed and described earlier for different types of nanoparticles [13–16]. The lower melting point compared to the bulk material is due to the large surface-to-volume ratio, which results in an increase in the surface free energy of the particles [17]. Several calculations were made to determine the melting point of nanoparticles with different size and shape [13,14,18–20]. For bulk gold the melting point is at 1064 °C [21], whereas for gold nanoparticles it can be found below this value. For non-spherical nanoparticles, a shape transformation into nanospheres can be observed as the nanoparticle reduces its surface energy due to the applied heat. The melting of both spherical and rod-shaped gold nanoparticles can be interpreted in terms of surface melting [22–25], whereby there is a small difference in the melting temperatures for the different facets [26–28]. For gold nanorods the surface melting is accompanied by the transformation into nanospheres, which is explained by Insawa et al. in Ref. [23] on the basis

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of surface tension considerations. The decrease of the aspect ratio depends on the thickness of the liquid layer, which depends on the temperature.

The effect of high temperatures on bare (without inorganic shell) gold nanorods was investigated experimentally by optical heating *via* laser pulses [29–33] or annealing solid-supported gold nanorods [34,35] using bulk-heating. Hu et al. investigated the heating of the nanorods between 180 °C and 500 °C using bulk-annealing [34]. They found that at 180 °C the nanorods coalesce into irregular shaped clusters and at 500 °C they coalesce into large spherical particles. Petrova et al. investigated the differences between the bulk- and ultrafast laser-induced heating of nanorods [35]. For bulk-heating they found that at 250 °C the solid-supported nanorods were converted into spheres. When laser-induced heating was performed in solution, the nanorods maintained their integrity up to 700 °C. It was suggested that the higher thermal stability of the nanorods heated by short laser pulses is a result of the quick release of heat into the surrounding liquid, i.e. the nanorods are not heated long enough to allow any significant structural change.

Several methods were published about protecting gold nanorods from the heat-induced shape deformation, which is crucial in some applications, e.g. in photothermal therapy [1,2] and photoacoustic imaging [36–38]. It was shown that embedding the nanorods into a titanium-oxide matrix [39], or coating with carbon [40] or other materials [7,25] can protect them from shape transformations during heating up to ~690 °C. For silica shells, however, the temperature related shape change of the core/shell nanoparticles upon bulk heating was investigated only up to 260 °C and for aspect ratios higher than 4 [41,42]. There are several methods to create a thin silica shell on gold nanorods (e.g. Refs. [43–45]) and it has been shown that the silica coating can increase the stability of the core particles when applying bulk heating up to 260 °C [41,42]. Gautier et al. [41] interpreted this shape-protecting effect of the shell on the basis of the higher melting point of silica compared to bulk gold. This allows the silica shell to sustain its shape and protect the core particles from coalescence hence acting as a mold for the core particles to preserve their rod shape. Nevertheless, there are no systematic studies available on the bulk heating of core/shell nanorods with different aspect ratio at high temperatures. In our study we use mesoporous silica-coated gold nanorods with AR ranging from 2.5 to 4.3. Based on our previous results [46] some degree of elasticity of the mesoporous shell is expected, but the question remains how the deformation of the core particle is influenced by the silica shell for different aspect ratios and how far the silica shell can sustain its integrity upon the shape change of the core particle?

In this work we investigate systematically how a mesoporous silica shell increases the stability of the gold core at high temperatures up to 900 °C. Gold nanorods with different aspect ratios were prepared and coated with a ca. 15 nm thick mesoporous silica shell. The particles were deposited onto solid substrates and these solid-supported nanoparticles were subjected to thermal treatment in an oven at different temperatures up to 900 °C. To investigate the changes in particle morphology and the plasmonic properties after annealing, scanning electron microscopy (SEM) and visible extinction spectroscopic measurements were carried out. Our results indicate that the silica coating effectively improves the thermal stability of the particles for all investigated aspect ratios. The larger aspect ratio nanorods however are more susceptible to deformation in agreement with surface energy considerations. It is confirmed that the conformal deformation of the silica shell upon annealing is dictated by the shape change of the core. For large aspect ratio nanorods, the mechanical stress during the deformation of the core results in the destruction of the silica shell.

2. Experimental section

2.1. Materials

Sodium borohydride, ReagentPlus® 99% ($NaBH_4$); tetrachloroauric (III) acid trihydrate, ACS reagent ($HAuCl_4 \cdot 3H_2O$); cetyltrimethyl ammonium bromide, SigmaUltra 99% (CTAB); 5-bromosalycilic acid, technical grade, 90% (5-BSA), tetraethyl orto-silicate, puriss, 99% (TEOS); L-ascorbic acid, ACS reagent 99% (AA); silver nitrate, 99.9999% metal basis ($AgNO_3$) and methanol, puriss. p.a., ACS reagent, reag. ISO, reag. Ph. Eur., ≥99.8% (MeOH) were purchased from Sigma–Aldrich. Sodium hydroxide, a.r. (NaOH) from Reanal and chloroform, reagent grade, ACS, ISO, stabilized with ethanol from Scharlau were used. All chemicals were used as received. For all experiments Milli-Q water (18.2 M Ohm cm^{-1}) was used.

2.2. Synthesis of mesoporous silica-coated gold nanorods

Au1, Au2 and Au3 gold nanorods with different aspect ratios were prepared by the seeded growth method similar to Ref. [43]. The aspect ratio of the nanoparticles was varied through the contents of the growth solution.

The seed solution was prepared by mixing 2.5 ml 0.001 M $HAuCl_4$, 2.5 ml H_2O and 5 ml 0.2 M CTAB. Then, 600 μl 0.01 M ice-cold $NaBH_4$ was injected. The resulting brownish solution was vigorously stirred for ~15 s, and then stirred at 45 °C for 15 min.

The Au1 nanorods (AR = 2.5) were synthesized by adding 40 μl seed solution to the growth solution containing 17 ml 0.0001 M $HAuCl_4$, 25 ml 0.2 M CTAB, 200 μl 0.04 M $AgNO_3$ and 238 μl 0.1 M AA.

The Au2 (AR = 3.0) and the Au3 nanorods (AR = 3.4) were prepared in a growth solution containing 50 ml 0.2 M CTAB, 100 μl 0.04 M $AgNO_3$, 50 ml 0.001 M $HAuCl_4$ and 700 μl AA. To 20 ml of this solution, in the case of Au2 rods 200 μl, in the case of Au3 rods 600 μl seed solution was added.

In the case of Au4 nanorods, with AR = 4.3 a different seeded growth method was used, according to Ref. [47]. The seed solution was made by mixing 0.5 ml 0.001 M $HAuCl_4$, 0.5 ml H_2O and 1 ml 0.2 M CTAB. Then, 0.12 ml 0.01 M ice-cold $NaBH_4$ was mixed with 0.08 ml water (room temperature) and added to this solution. After 2 min of vigorous stirring, it was left undisturbed for 30 min. The growth solution was prepared as follows: First, to 25 ml solution of 0.9 g CTAB and 0.11 g 5-BSA (30 °C), 0.96 ml 0.004 M $AgNO_3$ was added and stirred for 15 min. Then, 10 ml 0.001 M $HAuCl_4$ was put into the mixture, and stirred again for 15 min, followed by the addition of 0.07 ml 0.064 M AA and stirred for 30 s vigorously. Finally, 0.016 ml seed solution was injected.

The resulting solutions were left undisturbed overnight. The visible spectra of the nanoparticles were measured by using an Agilent 8453 spectrophotometer.

The silica coating procedure was carried out as reported in Ref. [48] with some modifications. First, 15 ml gold nanorod solution was centrifuged at 9500 rpm for 45 min at 28 °C and redispersed with 10 ml water. In the case of the Au4 nanorods, the dispersant CTAB − 5-BSA solution was changed with a 0.1 M CTAB solution by a prior centrifugation. The resulting solution's pH was set to ~10–11 with 0.1 M NaOH. Then, 3 × 15 μl 20:80 TEOS:MeOH mixture was added in 30 min intervals. This solution was stirred for 2 days, then centrifuged 5 times and redispersed in MeOH.

2.3. Preparation of monolayers on solid supports

The nanoparticle monolayers were first created at the water/air interface using a procedure reported by us earlier [48]. A