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Impact of the electron beam on the thermal stability of gold nanorods studied by environmental transmission electron microscopy

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ABSTRACT

In-situ transmission electron microscopy experiments are of great interest to nanoscience and nanotechnology. However, it is known that the electron beam can have a significant impact on the structure of the sample which makes it important to carefully interpret in-situ data. In this work, we studied the thermal stability of CTAB-stabilized gold nanorods under different gaseous environments in an environmental transmission electron microscope and compared the outcome to ex-situ heating experiments. We observed a remarkable influence of the electron beam: While the nanorods were stable under inert conditions when exposed to the electron beam even at 400°C, the same nanorods reshaped at temperatures as low as 100°C under ex-situ conditions. We ascribe the stabilizing effect to the transformation of the CTAB bi-layer into a thin carbon layer under electron beam irradiation, preventing the nanorods from deforming. When exposed to an oxidizing environment in the environmental transmission electron microscope, this carbon layer was gradually removed and the gold atoms became mobile allowing for the deformation of the rod. This work highlights the importance of understanding the phenomena taking place under electron beam irradiation, which can greatly affect in-situ experiments and conclusions drawn from these. It stresses that in-situ electron microscopy data, taken on measuring the temperature dependence of nanoparticle properties, should be carefully assessed and accompanied by ex-situ experiments if possible.

1. Introduction

When scaled down to nanometer size, many materials exhibit properties quite different from those of a bulk phase. This phenomenon has been the basis for the development of nanoscience and nanotechnology and has led to breakthroughs in various fields of research, ranging from physics and chemistry to medicine. In metal nanoparticles the confinement of electrons to the nanometer scale was found to result in exciting new phenomena. Among a plethora of different shapes and metals, gold nanorods (Au NRs) attracted a lot of scientific attention. Due to their tunable optical properties, catalytic activity, high chemical stability and bio-compatibility, Au NRs are considered for a wide variety of applications like drug delivery [1,2], sensing [3–6], photocatalysis [7], data storage [8–11] and hyperthermic cancer treatment [2,12–14].

Localized surface plasmon resonances (LSPRs) lie at the core of many applications as they lead to strong local electric field enhancements, especially at sharp corners and tips. Due to their anisotropic shape, Au NRs exhibit a (degenerated) transverse and a longitudinal LSPR. While the transverse resonance has a wavelength around 520 nm, the longitudinal LSPR can be tuned from the near-infrared to the visible part of the electromagnetic spectrum by decreasing the aspect ratio of the NR [15,16]. Thus, understanding the thermal stability of Au NRs is of crucial importance since a heat-induced deformation of the NRs leads to a decrease in aspect ratio and consequently affects their optical properties [17–19]. It is generally established that the NR shape becomes unstable upon heating to temperatures many hundreds of degrees below the bulk melting temperature (1064°C), sometimes even as low as 100°C [20,21]. The thermal stability can be enhanced by an inorganic, possibly mesoporous, coating such as silica that hinders the diffusion of surface atoms [22–25]. Despite the increasing interest in anisotropic NPs as (photo)catalysts for oxidation and hydrogenation reactions, to the best of our knowledge, no extensive research has been performed to study their thermal stability under different gaseous

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environments and thus more realistic catalytic conditions.

Transmission electron microscopy (TEM) has played a pivotal role in investigating nanomaterials' structures and linking properties associated with the nano length scale(s) of materials to their bulk behavior. Furthermore, the development of environmental TEM (ETEM), with gaseous environments in the sample chamber and heating elements, allows for various experiments to be performed in-situ, revealing sample transformations in real time and under a wider range of conditions [26–29]. In addition, we chose ETEM for studying the thermal stability of Au NRs in different environments. However, when choosing an electron-beam technique, one challenge is to understand and/or minimize the influence of the electron beam on the measurements.

In recent years, more attention has been drawn to the potentially strong effects that the electron beam can have on the processes studied in-situ (E)TEM investigations. Apart from well-known e-beam induced damages to the sample's structure during regular TEM imaging [30], in-situ TEM studies with or without heating under vacuum, gas-phase and liquid phase conditions, brought about additional challenges. It was recently shown, for example, that the electron beam leads to an increased dislocation activation during in-situ TEM experiments investigating tensile straining of aluminum and gold films [31]. Furthermore, the electron beam ionizes gas molecules which can lead to an increased reactivity, as seen for the oxidation of carbon nanotubes [32] and Pt nanoparticles [33] observed by ETEM. In the case of the recently developed liquid phase TEM, the electron beam effects are perhaps the most prominent, as it was repeatedly argued that the electron beam leads to radiolysis of water and a formation of various reducing and oxidizing species [34]. Therefore, it is ever more important to carefully assess the impact of the electron beam on the samples' behavior.

In our experiments, we observed that the electron beam significantly increased the thermal stability of Au NRs, through the formation of a protective carbon layer formed almost instantly by high-energy electron beam induced pyrolysis of the organic surfactant surrounding the Au NRs. Owing to the use of an ETEM, an oxidizing environment could be introduced which led to the gradual removal of the carbon layer. Our research shows that an electron beam and the presence or absence of certain gasses can have a large impact on a sample during in-situ TEM experiments and calls for critical assessment of in-situ TEM data and a need for comparison with ex-situ experiments before any conclusions about the sample structure and/or behavior can be drawn.

2. Experimental

2.1. Synthesis of Au NRs

The following chemicals were used: gold(III) chloride trihydrate (99,9%, CAS nr: 16961-25-4), cetyltrimethylammonium bromide (98%, CAS nr: 57-09-0) and L-ascorbic acid (99%, CAS nr: 50-81-7) from Sigma Aldrich. Sodium borohydride (98%, CAS nr: 16961-66-2) and silver nitrate (99,9%, CAS nr: 7761-88-8) were purchased from Alfa Aesar. All synthesis steps were performed using purified Milli-Q water (Merck, 18.2 MΩ).

The Au NRs were grown via a silver-assisted seeded growth method described by Liz Marzán et al. [35]. This method consists of preparing the growth solution and the gold seeds separately before adding the seeds as nuclei to the growth solution. First the gold seeds were synthesized by preparing 10 mL of an aqueous solution containing 0.25 mM $HAuCl_4$ and 0.1 M cetyltrimethylammoniumbromide (CTAB). Successively the solution was vigorously stirred at room temperature, while 0.6 mL of freshly prepared 10 mM $NaBH_4$ solution was added. The reaction mixture was stirred for 2 minutes and aged for 5–10 minutes before further use. Second, 500 mL of the aqueous growth solution containing 0.5 mM $HAuCl_4$, 0.1 M CTAB, and 0.12 mM $AgNO_3$ was prepared. Then the solution was brought to pH 3-3.5 by addition of HCl. Throughout the synthesis the solution was stirred gently at 30° C. In order to reduce the gold, 3.5 mL of 78.8 mM ascorbic acid was added, followed by the addition of 0.6 mL freshly prepared gold seeds. The reaction mixture was gently stirred overnight.

To grow the Au NRs larger than reported by Liz Marzán et al. [35] more reducing agent was added in 5 successive steps with a 2 h interval. In each step 0.31 mL of 78.8 mM ascorbic acid was added and the reaction mixture was again gently stirred overnight. The mixture was then washed twice by centrifugation at 6500 RPM for 1 h. In order to prevent aggregation of the NRs, the CTAB concentration was kept at 8 mM. The average length and width of the obtained NRs were 64.5 nm and 18.6 nm, respectively.

2.2. Ex-situ heating experiments

Two consecutive droplets (the second one was placed after evaporation of the first drop) of the Au NRs' solution were dried on microscope glass slides (76 × 26 mm, Thermo scientific, Menzel-Gläser) and placed in a preheated static air oven (Carbolite) at either 100°, 150°C or 200°C for one hour. The extinction of the heated NRs on the microscope slide was measured with an empty glass slide as reference. The extinction measurements were performed on a Bruker Vertex 70 FT VIS-IR spectrometer. The Au NRs were then redispersed in H_2O before placement on a TEM grid. The TEM measurements of the ex-situ treated samples were performed on a FEI Tecnai 12 microscope operated at 120 kV.

2.3. In-situ heating experiments

For the experiments in vacuum, a drop of the CTAB-coated Au NRs dispersion was dried on a TEM heating chip consisting of several silicon nitride windows surrounded by a coiled Pt wire. The TEM heating chip was then placed in a DENS solutions heating holder and heated resistively in-situ to 400°C by increasing the temperature by 50°C every 20 s. The TEM imaging in this experiment was performed with a FEI Tecnai 12 microscope operated at 120 kV. During the heating to 400°C and during 1 h at that temperature one selected window of the heating chip was exposed to the electron beam, while other areas were imaged afterwards.

For the ETEM experiments, the Au NRs samples were supported on a Mo grid mesh with a holey carbon supporting film. A mesh with deposited NRs was fixed onto a TEM heating holder and transferred to an ETEM (FEI Tecnai F20 transmission electron microscope equipped with a specially designed environmental cell [36]) operated at 200 kV. Gaseous O_2, N_2, CO, and mixtures of these gases were introduced into the environmental cell and the samples were observed at room temperature, at 100°C, 200°C, 300°C, and at 400°C. The heating rate of the sample was 10°C min^{-1}. ETEM observations were started 60 minutes after reaching the target temperatures. The nominal impurities in all the gases were less than 0.005 vol%. Residual gases in the ETEM were measured using a quadrupole mass spectrometer. The total pressure of residual gas was about $6.5 \cdot 10^{-2}$ Pa, of which the partial pressures of constituent gases were H_2O: $5.9 \cdot 10^{-2}$ Pa, N_2: $0.3 \cdot 10^{-2}$ Pa, O_2: $0.2 \cdot 10^{-2}$ Pa, and CO_2: $0.1 \cdot 10^{-2}$ Pa. For the ETEM experiments performed on the Au NRs, the pressure of different gases was varied between 50 Pa and 200 Pa to ensure that the pressure is much higher than that of the residual gases and vacuum. We also observed the NRs under vacuum at the above mentioned temperatures in the ETEM. ETEM images were acquired using small electron beam currents lower than 1.0 Acm^{-2}. High resolution TEM images were obtained by a Titan ETEM G2 (FEI) operated at 300 kV.

Energy dispersive X-ray analysis was performed on a JEM-ARM200F (JEOL) microscope operated at 200 kV. Electron energy-loss spectroscopy was performed on a Titan ETEM G2 (FEI) microscope operated at 80 kV.