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Monochromated, spatially resolved electron energy-loss spectroscopic measurements of gold nanoparticles in the plasmon range

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ABSTRACT

Gold nanoparticles show optical properties different from bulk material due to resonance phenomena which depend on local structure and geometry. Electron energy-loss spectrometry (EELS) in scanning transmission electron microscopy (STEM) allows the spatially resolved measurement of these properties at a resolution of few nanometers. In this work, the first monochromated measurements of gold nanoparticles (spheres, rods and triangles) are presented. Due to the improved energy resolution of about 0.2 eV, surface plasmon excitations at energies below 1 eV could be accurately measured from raw experimental data.

1. Introduction

Metal nanoparticles (Me-NPs) in general and gold nanoparticles (Au-NPs) in particular, are attracting strong attention in research and application as they show a large variety of optical behaviour. For example, ruby-coloured stained glass as already used in the 17th century owes its colour to Au-NPs as a pigment (Kerker, 1985). Nowadays, Me-NPs are used as sensors for scanning near-field optical microscopy (SNOM or NSOM) (Kalkbrenner et al., 2001), surface-enhanced Raman scattering (SERS) (Kneipp et al., 1997; Xu et al., 1999), or chemical and biomolecular sensing (Nath and Chilkoti, 2002; Sun and Xia, 2002). The response of a nanoparticle to an electro-magnetic wave depends on the particle's size and shape (Link and El Sayed, 1999; El Sayed, 2001; Evans et al., 2007) as well as on the local dielectric environment (Jensen et al., 1999), offering numerous ways for custom-tailoring the behaviour to the needs of particular applications. Additionally, coupling to neighbouring nanoparticles also has a strong influence (Atay et al., 2004; Aizpurua et al., 2005; Bryant et al., 2006).

Optical properties of Au-NPs have been intensively investigated by many optical spectroscopic techniques based on absorption, reflection or scattering of visible light at the nanoparticles. However, due to the lack of spatial resolution of these techniques – the sampling volume being larger than the particles – the results are usually averaged over a whole set of particles. Even if this set is monodispersive with respect to size and shape of the particles, differences due to local variations in surface geometry of individual (anisotropic) particles such as rods, tripods or triangles cannot be detected. Optical near-field measurements improve the spatial resolution to 10–50 nm and allow spatially resolved measurements of larger structures, e.g. nano-wires and rods (Klar et al., 1998; Hillenbrand and Keilmann, 2001; Ducourtieux et al., 2001; Hohenau et al., 2005).

Alternatively, electron energy-loss spectroscopy (EELS) can be used to probe dielectric properties of a material. A beam of fast incident electrons can be understood as a time varying electric field which induces an electric field in the sample. The related loss of energy in the primary beam is connected to the dielectric function ε of the specimen. While EELS allows ε to be determined over a large energy scale from zero to several hundredths of eV, optical properties of a specimen for visible light are contained in the energy range between 1.65 and 3.25 eV which corresponds to the wavelengths of 750 nm and 381 nm, respectively. Optical absorption in Me-NPs can be understood in terms of surface plasmon excitations. In general, a plasmon is the collective oscillation of the conducting electrons, and a surface plasmon is an oscillation propagating along the specimen surface. In spectroscopy, a plasmon peak can be detected at the energy of the resonance frequency of this oscillation within the Me-NP. EELS in a transmission electron microscope (TEM) and scanning TEM (STEM) has been used to measure plasmons of nanoparticles in spatially

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resolved manner (Batson, 1982; Wang and Cowley, 1987), and more recently, surface plasmons of Ag-NPs and Au-NPs have been two-dimensionally mapped (Bosman et al., 2007; Nelayah et al., 2007). STEM microscopes allow atomic resolution imaging by detection of strongly scattered electrons using a high-angle annular dark-field (HAADF) detector. However, signal delocalization limits the spatial resolution of EELS at low energy-losses (Muller and Silcox, 1995) and EELS spectra from closely spaced composite structures may even be dominated by the delocalized signal (Couillard et al., 2008).

A major experimental difficulty in measuring surface plasmons of Me-NPs by EELS is the strong peak of all elastically interacting primary electrons, the so call zero-loss peak (ZLP). This peak essentially resembles the measured energy distribution of the primary electron beam, and thus defines the energy resolution of the system which is conventionally measured as the width of the ZLP at half of its intensity—full-width at half-maximum (FWHM) value. The limited energy resolution of first generation systems is the reason that only few experimental EELS spectra of gold with energies below 3 eV exist, despite the fact, that gold has been intensively studies by EELS (in transmission and also in reflection scattering geometry) in the past (Sueoka and Fujimoto, 1965; Powell, 1968; Lässer et al., 1981; Yoshikawa et al., 1995; Kwei et al., 1997; Werner, 2006; Werner et al., 2007).

New interest in low-loss EELS below 5 eV was triggered by the development of electron source monochromators for TEM (Tiemeijer, 1999; Terauchi et al., 1999; Mook and Kruit, 2000), because not only the energy-spread of the beam could be improved, but also the long extending tails of the ZLP are diminished in comparison to a cold field-emission gun of similar FWHM energy spread. Furthermore, the energy distribution of the beam of cold field-emission gun, measured as the ZLP, is asymmetric whereas the ZLP tails of a monochromated beam are symmetric which gives a strong advantage for ZLP removal procedures, especially in the close low-loss range (Kimoto et al., 2005). Thus, monochromated measurements allow reliable detection of peaks for energy-losses below 2 eV which cannot be achieved by mathematical improvements of energy resolution such as maximum-likelihood deconvolution.

2. Experiment

All EELS measurements were performed with the monochromated Tecnai TF20 microscope (FEI Company) installed at the Graz University of Technology. This 200 kV field-emission microscope ($C_c = C_s = 1.2$ mm) is optimized for high energy resolution EELS measurements (Kothleitner and Hofer, 2003), using an improved high tension tank, a Wien-filter monochromator (Tiemeijer, 1999), an active triaxial magnetic field compensation, and the High Resolution Gatan Imaging Filter (Brink et al., 2003) with an UltraScan CCD camera (2048 pixels × 2048 pixels, 16-bit dynamic range)(Riegler, 2008). EELS spectrometer dispersions used in this work were calibrated by acquisition of spectra of alumina and taking the bulk plasmon peak maximum at 15.0 eV as a reference (Egerton, 1996). For the use in STEM mode, the microscope is also equipped with bright-field and dark-field detectors (Gatan), and with a HAADF detector (Fischione). In STEM mode, the DigiScan II beam control (Gatan) is used, and all spectra are acquired within the DigitalMicrograph (Gatan) software.

The gold nanoparticles were synthesized as follows. Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O > 99.5\%$) was purchased from Carl Roth GmbH. Trisodium citrate dihydrate (99%) and sodium chloride (NaCl; 99.5%) were obtained from Merck. All chemicals were used as received and purified water was used for the reactions. The experimental method was a modification of the conventional citrate reduction of gold salt in water (Turkevich et al., 1951; Riegler, 2005). The solution consisted of 1 mL $HAuCl_4$-solution (2.5 mM), 25 μL sodium citrate (0.1 M), 0.5 mL sodium chloride (5 M) and 8.5 mL water. One drop of particle solution was put on a carbon-coated copper grid, and the liquid was allowed to evaporate at room temperature.

Three major types of Au-NPs were identified in this sample: Spheres with a diameter between 35 and 45 nm, rods with a diameter between 18 and 22 nm and a length between 100 and 800 nm, and flat triangles with a side length between 40 and 80 nm and a thickness between 15 and 20 nm. Fig. 1 shows HAADF images of the specimen, acquired with a monochromated electron probe. The diameter of the probe was 2.8 nm diameter, measured as FWHM of the beam profile, giving a probe current of 131 pA (Rechberger, 2007).

Monochromated EELS spectra were recorded from the indicated areas with the beam quickly scanning the square area to reduce carbon contamination during the measurement. Two spectra were acquired at each location. For the first spectrum, an image filter energy shift was chosen such, that the high intense zero-loss peak (ZLP) was positioned just outside the area of the CCD camera, preventing overexposure. The second spectrum was acquired with the whole ZLP centred on the CCD. In both cases, exposure times

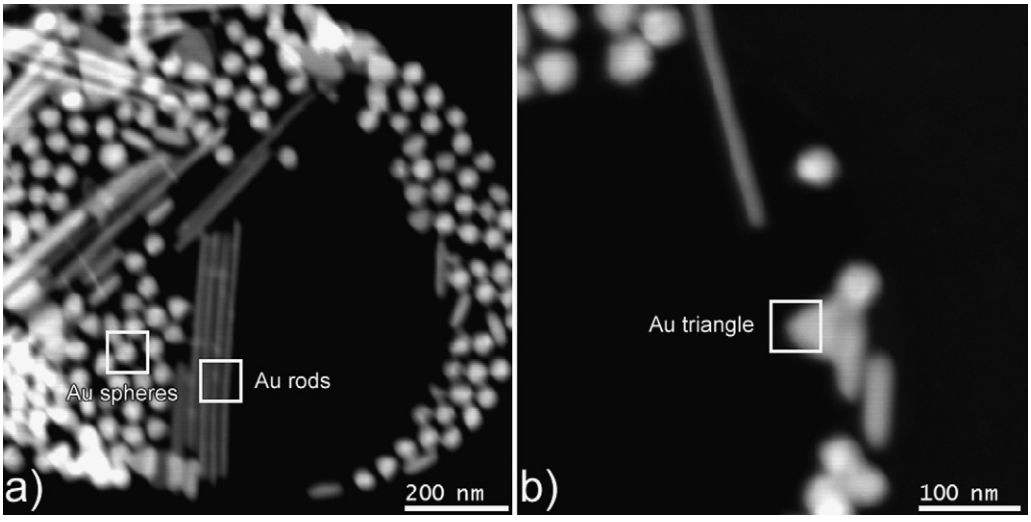

Fig. 1. STEM HAADF images of Au-NPs showing the positions of EELS acquisition.