EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Graphene oxide in nanoparticle fragmentation – quenching instead of passivation	**Experiment number:** SC5265
Beamline: ID9	**Date of experiment:** from: 15/06/2022 to: 20/06/2022	**Date of report:** 1/3/2023
Shifts: 15	**Local contact(s):** M. Levantino	*Received at ESRF:*

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Goal: Metallic nanoparticles in a transition to the quantum state gain functional properties, which depend delicately on size or shape. For example, gold nanoclusters that are smaller than 3 nm show significant catalytic activity (e.g. to oxidize CO). In the quest for producing surfactant-free clusters of this size range (1-3 nm) we investigate the process of laser fragmentation by ultrashort light pulses in water [1] and show that the surfactant-free metal clusters showed a luminescence that has only been known before for gold-ligand charge transfer systems [3]. However, the laser-induced fragmentation and growth processes and mechanisms that occur on ps- to µs-time scale remain elusive. In particular, the inhibition of growth processes shortly after or directly during the cluster formation remains challenging. Therefore, a physical interface, such as graphene (or its water-soluble counterpart graphene oxide, GO [4]) may prevent surface poisoning.

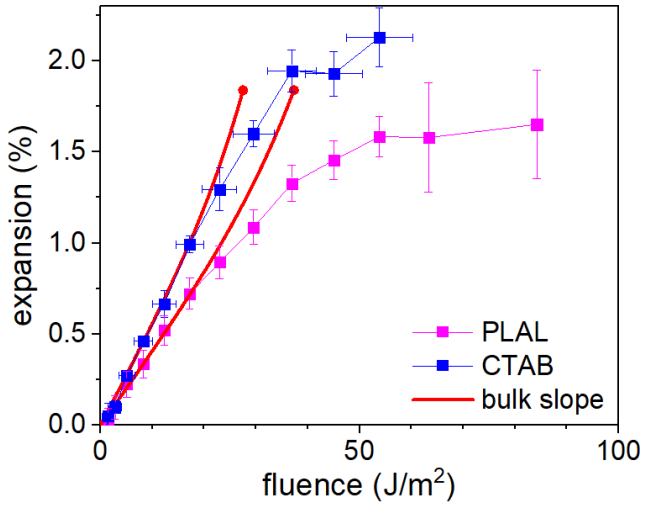

Fig. 1: *Lattice expansion of the gold colloids of about 60 nm diameter at 60 ps as function of fluence F as observed by the angular shift of the (111) powder reflection. The thermal lattice dynamics of the ablation produced colloid (PLAL, pink) has been compared to chemically produced particles with strong ligand stabilization (CTAB, blue). The slope is compatible with the change of lattice spacing as function of temperature, assuming bulk-like expansion coeffient and latent heat and the absorption cross section of the colloids in water [2,7]. The bullet at the end of the calculated lines marks F_0.*

In the present beamtime SC5265 we have performed a pump-probe experiment on ligand-free gold colloid (produced in the lab by laser ablation [3]) with and without addition of GO nanosheets. Direct educt particle adsorption on GO is inhibited under the applied pH conditions. The experiment applied single-shot irradiation by 400 nm laser pulses of 1 ps duration, which are subject to less bleaching than the frequently used resonant wavelength of 532 nm at the plasmon resonance [4]. Scattering from the suspension jet was collected in a small angle (SAXS) and wide-angle (WAXS) range. The spectral emission line at 15 keV from the in-vacuum undulator U17 was used in full. The reduced bandwidth due to the EBS allowed resolving even the dynamics in wide-angle scattering. Data has been analyzed to derive: (i) the lattice state and (crystalline) temperature of the colloids, (ii) the destruction of the educt particles and (iii) the formation of new clusters in the nm range as function of delay and calibrated laser fluence.

The laser fluence plays the role of dosing the energy uptake by each individual particle, a quantity, which in principle can be guessed from the absorption cross section. We could verify that lattice expansion, as indicator for lattice temperature will change linearly with fluence below some threshold F_0 in the range of 40-50 J/m^2. Above that, particle crystallinity is lost, while the remaining crystalline particle do not expand further than the expected value at the melting point (about 1.8 %, see fig. 1). Thus, we can pinpoint a critical fluence F_0 for reaching the melting point, which will allow to scale the absorbed energy for even higher fluences.

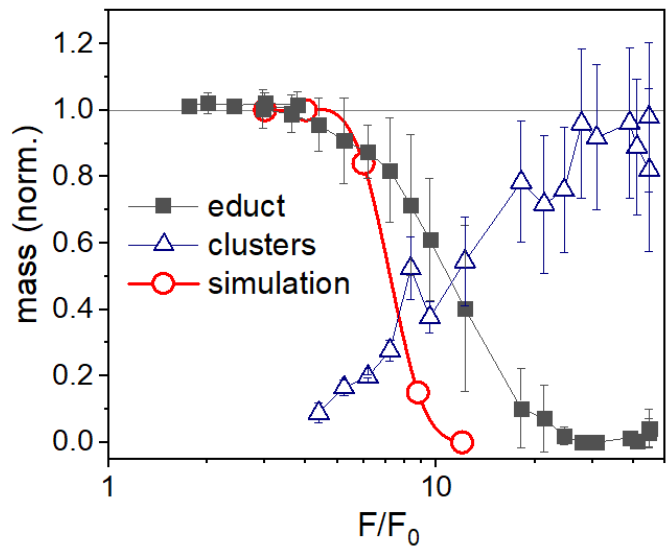

Fig. 2 a: *Masses of the CTAB educt particle (■), the nm-sized clusters (Δ) as function of the reduced fluence F/F* as derived fitting the difference scattering, adapted from [6]. The pink open symbols represent the result from theoretical investigations [5].*

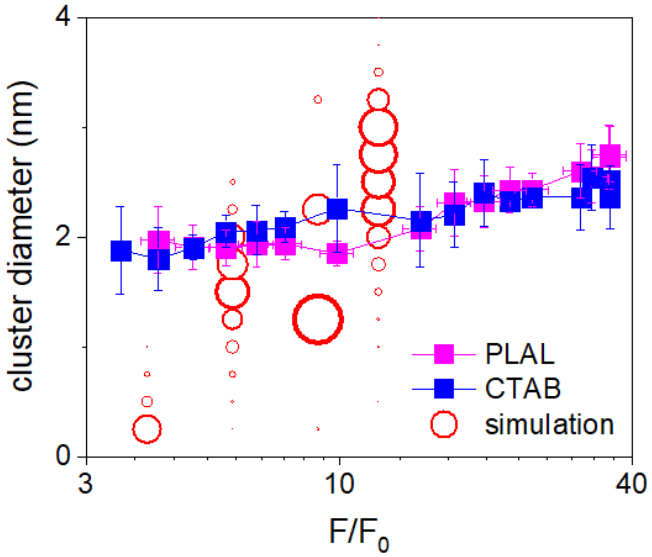

Fig. 2 b: *Mean cluster diameter (■) of the products from CTAB (blue) and PLAL (pink) particles as function of the reduced fluence F/F$_0$, adapted from [6]. The open pink circles are cluster size distributions as derived from the simulations [5], where the circle size encodes the occupancy in the distribution.*

Thus, the thermal and structural evolution of the nanoparticles can be resolved quantitatively. Indeed, the particles melt and recrystallize within the heat dissipation times among further relaxations [1] within the time resolution of 60 ps. At a delay of 1 µs the system has come to an intermittent rest and the products can be analyzed. It is intriguing to see that just above the melting transition the particles would eventually reform the initial educt without important damage (fig. 2 a). Only at a reduced fluence F/F_0 of about 4 some damage is found and educt start to be reduced in size and vanish at about 7-8. This high value means that the evaporation temperature has been reached ($F/F_0 = 3.7$) and even half of the latent heat for evaporation has been provided. In fact, precise theoretical predictions in simulations [5] predict exactly that behavior and reproduce the observed nanosized clusters as function of fluence (fig. 2 b). Together, we can paint the picture of a thermally induced phase explosion of gold as a spinodal process [6]. Evaporation itself would not produce the rates necessary to consume the particles in this short delay span (the particles cool down within < 30 ns [1]).

Introduction of GO at low concentration (300 mg/l, in order to avoid direct energy deposition) does in first place not change this process of fragmentation. First, no additional GO signal is found at this concentration, as layering has been reduced through ultrasound defoliation. Energy uptake in the gold particles as well as fragmentation thresholds stay constant. Nevertheless, SAXS shows very distinct changes at $F/F_0 > 10$, where a violent phase explosion happens. This is attributed to the confining effect of the GO sheets, which due to the negative charges do not absorb clusters, but limit the expulsion of material into the water bulk. Thus, in the presently used form of GO no cluster stabilization has been found, but rather a caging effect.

References:

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