

Barrierless growth of precursor-free, ultrafast laser-fragmented noble metal nanoparticles by colloidal atom clusters – A kinetic in situ study

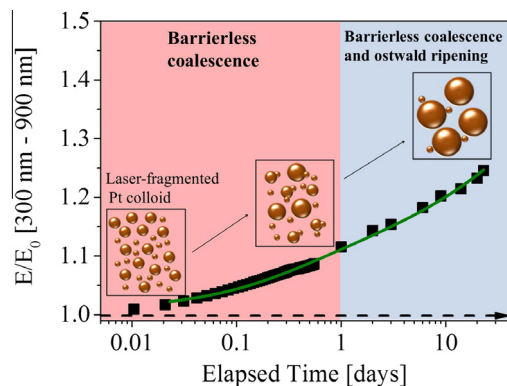


Sandra Jendrzej^a, Bilal Gökce^a, Vincenzo Amendola^b, Stephan Barcikowski^{a,*}

^a Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitaetsstr. 7, 45141 Essen, Germany

^b Department of Chemical Sciences, Università di Padova, 1 Via Marzolo, I-35131 Padova, Italy

GRAPHICAL ABSTRACT



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ABSTRACT

Unintended post-synthesis growth of noble metal colloids caused by excess amounts of reactants or highly reactive atom clusters represents a fundamental problem in colloidal chemistry, affecting product stability or purity. Hence, quantified kinetics could allow defining nanoparticle size determination in dependence of the time. Here, we investigate in situ the growth kinetics of ps pulsed laser-fragmented platinum nanoparticles in presence of naked atom clusters in water without any influence of reducing agents or surfactants. The nanoparticle growth is investigated for platinum covering a time scale of minutes to 50 days after nanoparticle generation, it is also supplemented by results obtained from gold and palladium. Since a minimum atom cluster concentration is exceeded, a significant growth is determined by time resolved UV/Vis spectroscopy, analytical disc centrifugation, zeta potential measurement and transmission electron microscopy. We suggest a decrease of atom cluster concentration over time, since nanoparticles grow at the expense of atom clusters. The growth mechanism during early phase (<1 day) of laser-synthesized colloid is kinetically modeled by rapid barrierless coalescence. The prolonged slow nanoparticle growth is kinetically modeled by a combination of coalescence and Lifshitz–Slyozov–Wagner kinetic for Ostwald ripening, validated experimentally by the temperature dependence of Pt nanoparticle size and growth quenching by iodide anions.

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* Corresponding author.

E-mail addresses: sandra.jendrzej@uni-due.de (S. Jendrzej), bilal.goekce@uni-due.de (B. Gökce), vincenzo.amendola@unipd.it (V. Amendola), stephan.barcikowski@uni-due.de (S. Barcikowski).

1. Introduction

Although colloidal noble metal nanoparticles are essential building blocks in catalysis [1,2] and biomedicine [3], unintended post-synthesis by coalescence and ripening presents a fundamental problem since particle size quality or modality changes over time affecting reproducibility along downstream processing and application. Even commercial metal nanoparticles with nominal multi-nanometer sizes often contain small particle fractions out of specification [4]. Aqueous metal nanoparticle synthesis is naturally based on precipitation chemistry which relies on seed-growth, so that in situ studies contribute to understand the origin and kinetics of this growth [5,6], naturally expected during synthesis, but usually disregarded on longer time scales. The nanoparticle alteration may be prevented or decelerated when particles are capped by electrostatic or steric ligands [7]. However, ligand-covered nanoparticles are mostly undesired for applications such as heterogeneous catalysis due to reduced adsorption efficiency and reduced catalytic activity [8,9]. An established method to synthesize pure nanoparticles is possible via pulsed laser ablation of a bulk metal target in liquids [10–14]. Due to electrostatic stabilization caused by surface oxidation in the surrounding liquid, the nanomaterials are colloidally stable although they are synthesized without any surfactants and are free of impurities or residual precursors [15]. In order to reduce the particle size and to generate monomodal and narrow particle size distributions, a further laser fragmentation step was frequently carried out in last years [11,16,17]. In particular, the resulting particle size of post irradiated nanoparticles depends strongly on the laser fluence and pulse duration [17,18]. Hashimoto et al. have proposed different mechanisms for the size reduction of nanoparticles, including coulomb explosion, surface evaporation and near-field ablation [17]. During the laser fragmentation process, both smaller nanoparticles (>2 nm, with well-defined plasmon resonance) and atom clusters (few atoms to 2 nm, quantum confined and typically without plasmon resonance band) may be generated [19–21]. Since ligand-free metal atom clusters are highly reactive and possess high surface energy due to unoccupied binding sites, they exhibit among all nanoparticles the highest thermodynamic tendency to grow [7], which is mostly (depending on nanoparticle material and liquid) in contrast to ligand-covered atom clusters [19,21–23]. Recently, Giorgetti et al. have found evidence for laser-generated silver clusters in water, and the Ag_4^{2+} species were determined to be stable during pulsed laser ablation [24]. Furthermore, the successful synthesis of ligand-free, oxidized gold atom clusters in water via controlled size reduction of gold nanoparticles by pulsed laser-induced oxidative fragmentation has been reported [16]. Despite both successful cluster syntheses, atom clusters generated in water without addition of any surfactants are unstable and tend to grow, with yet almost unexplored kinetics. In previous works, the growth kinetics of particulate fragments during laser fragmentation in the timescale of picoseconds were investigated in detail [17,25,26]. Hashimoto et al. showed that coalescence and coagulation takes place in the cavitation bubble during laser-fragmented nanoparticle formation via heating-evaporation mechanism [17,27]. However, studies that elaborate the growth behavior of laser-fragmented nanoparticles in presence of atom clusters in a time regime of minutes to several days are almost unexplored and are required to extract kinetic constants. Mafuné et al. investigated the growth kinetics of ligand-covered, laser-fragmented gold atom clusters in the presence of nanoparticles in a time regime of 0–9 h by varying the laser fluence and sodium dodecyl sulfate concentration (SDS) [28]. They found that the coalescence between atom clusters and nanoparticles is reduced in highly concentrated sodium dodecyl sulfate solutions [28]. While the growth kinetics of these ligand-covered, laser-fragmented gold atom clusters have

been investigated in detail [28], a determination of the growth dynamics and kinetics of ligand-free metal nanoparticles in presence of atom clusters is still missing and yet to be provided since nanoparticles with constant particle sizes are crucial for nanoparticle application.

In this paper, the growth kinetics of ligand-free Pt nanoparticles in the presence of atom clusters in water are investigated spectroscopically in situ and analytically ex situ on a time scale of minutes to 50 days after the generation of nanoparticles by laser-induced fragmentation. In addition, the growth mechanism and possible surfactant-free growth quenching methods by charge delivery are determined. Our study is extended to the elements Au and Pd, which have higher and lower oxidation potential than Pt and are highly relevant for biomedical applications and catalysis.

2. Materials and methods

Ligand-free nanoparticles are produced by pulsed laser ablation in liquids (PLAL). An Nd:YAG laser (Ekspla, Atlantic) with a pulse duration of 10 ps, a repetition rate of 100 kHz, a pulse energy of 156 μJ and a laser wavelength centered at 1064 nm is used. The laser beam is focused with an f-theta lens (focal length of 100.1 mm) to ablate the noble metal targets in aqueous solutions of 20 $\mu\text{mol/L}$ NaBr (99.99%, Sigma Aldrich) in a self-constructed flow through chamber with a liquid layer of 6 mm (Fig. 1(a)). The ablated Pt mass is determined by gravimetric measurement of the Pt target before and after laser ablation resulting in Pt concentrations of 130–170 $\mu\text{g/mL}$. Laser ablation of a Pt bulk target in water results in a bimodal size distribution [29]. Hence, NaBr salt is dissolved in the liquid medium at micromolar ionic strength in order to induce a size quenching of nanoparticles by delivering surface charge density and to reduce the bimodality, as shown in Fig. S1 [30,31]. Subsequent pulsed laser fragmentation in liquids (PLFL) (Ekspla, 10 ps, 78 μJ , 100 kHz, 532 nm) is performed for 30–40 min with a colloid concentration of 130–170 $\mu\text{g/mL}$ (30 mL) in a stirring vessel in order to generate small nanoparticles and atom clusters (Fig. 1(a)). The optical absorption and subsequent coulomb explosion of nanoparticles generates smaller nanoparticles and atom clusters [17,20,21]. To cut-off particle diameters or non-irradiated aggregates >10 nm, a subsequent centrifugation step is carried out (Hettich, Universal 32, 18,000 rpm, 23,904 g, 5 min). The Pt concentration after centrifugation is determined by reference to a UV/Vis calibration curve (Fig. S2) of laser-fragmented Pt colloid dilution series. Colloidal solutions are stored at defined temperature (20 °C) to ensure that the ambient temperature does not have an influence on the particle growth. Sizes were measured one day after synthesis by analytical disc centrifugation (ADC, CPS instruments, DC 24000, particle detection at 405 nm) of centrifuged and not-centrifuged, laser-fragmented and laser-ablated Pt colloid particles, as shown in Fig. S3. Growth kinetics of laser-fragmented Pt nanoparticles and atom clusters are investigated dynamically via in situ long term measurements by analytical disc centrifugation, zeta potential measurement (Malvern Instruments, Malvern Zetasizer) and extinction-calibrated optical absorption spectroscopy (Thermo Scientific, Evolution 201). Time resolved transmission electron microscopy (TEM, Phillips, CM12) was used to visualize the particle alteration.

3. Results and discussion

The insert in Fig. 1(b) indicates a significant difference of the optical properties of nanoparticle colloids via Tyndall effect produced by laser ablation and subsequent laser fragmentation. The Tyndall effect of laser ablated nanoparticles is very intense, but in contrary most of the visible light of laser-fragmented sample

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