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Ligand-free gold atom clusters adsorbed on graphene nano sheets generated by oxidative laser fragmentation in water

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ABSTRACT

Over three decades after the first synthesis of stabilized Au_{55}-clusters many scientific questions about gold cluster properties are still unsolved and ligand-free colloidal clusters are difficult to fabricate. Here we present a novel route to produce ultra-small gold particles by using a green technique, the laser ablation and fragmentation in water, without using reductive or stabilizing agents at any step of the synthesis. For fabrication only a pulsed laser, a gold-target, pure water, sodium hydroxide and hydrogen peroxide are deployed. The particles are exemplarily hybridized to graphene supports showing that these carbon-free colloidal clusters might serve as versatile building blocks.

1. Introduction

Gold clusters have attracted much attention because of their optical properties. Instead of plasmonic gold nanoparticles with metallic character, ultra-small gold particles show quantization of electronic energy levels [1,2]. The size threshold for significantly quantum-sized gold clusters can be estimated by the jellium model to be ~2 nm assuming complete defect-free filling of the valence shells [3]. At much higher number of gold atoms, energy level spacing eventually becomes comparable to available thermal energy so that this transition size regime connects atomic and metallic behavior, as can be seen by proto plasmonic fluorescence properties. These clusters are of particular interest in a variety of application fields, e.g. as optical limiters [4], for heterogeneous catalysis [5–7] or as fluorescent markers [8–10], where gold clusters have already been successful applied, but till now only synthesized with reduction chemistry and stabilizing ligands. Gold particles smaller than 2–3 nm show no surface plasmon resonance in the extinction spectra and have non-linear optical properties [11,12].

Although fluorescence of gold clusters has been shown by several groups, it is still unclear if fluorescence origins from the gold itself or the orbital coupling when organic molecules are adsorbed on particle surface [13]. Recently, Lin et al. showed that fluorescence properties of gold clusters are strongly affected by the ligands attached to gold atom clusters surface [14]. Besides these clusters are known to be efficient for homogeneous and especially heterogeneous catalysis [15] where the catalytic activity depends on the size of the particles [16]. Availability of colloidal gold atom clusters free of organic molecules would allow the study of optical or catalytic properties in this atom–metal transition particle size regime without cross-effects by surface absorbed ligands.

In 1993, Fojtik and Henglein reported for the first time the laser-based synthesis of inorganic nanoparticle colloids [17]. Since the 2000s laser ablation and fragmentation in liquids became a research field growing by factor 15 in a decade [18] allowing to produce colloids of high purity via a facile synthesis route that fulfills the twelve principles of green chemistry [19,20]. Gold nanoparticles, for example, are obtained simply by focusing a laser beam on a gold target placed in water without any reactants [21]. These gold nanoparticles show a high reactivity due to their pure (ligand-free) surface and can be used, e.g. for bio-conjugation with a variety of molecules [22–24] or sorption on supporting particles [25]. Also bimetallic nanoparticles colloids can be fabricated by laser ablation and fragmentation in liquid, e.g., silver/gold [26]. As a drawback,

Abbreviations: TEM, transmission electron microscopy; HR-TEM, high resolution transmission electron microscopy; ADC, analytical disc centrifuge; DLS, dynamic light scattering; GNS, graphene nano sheets.

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laser-generated particles have a wide size distribution compared to chemically synthesized ones [27,28]. To reduce this scientific drawback of polydispersity, size quenching effects by adding salts or ligands [29] can be used, resulting in monodisperse gold colloids. An alternative size reduction method is post irradiation with ultrashort laser pulses avoiding contaminations by additives [30–32].

It is known that pulsed laser irradiation of gold colloids with laser fluence of 0.05–0.5 J/cm^2 may cause a reduction of particle diameter down to a size limit of 4 nm [33]. Yet, only the addition of organic surfactants gave access to particle sizes smaller than 4 nm via the laser fragmentation route [34,35], but unfortunately the employed stabilizers cover the final gold cluster surface and are difficult to remove quantitatively.

2. Materials and methods

2.1. Laser ablation and fragmentation

In our experiments, we firstly generated educt particles by laser ablation of a gold target in an ablation chamber filled with deionized water (Millipore pH ~5–6) using a picosecond pulsed Nd:YAG laser (Ekspla, Atlantic Series, 10 ps, 100 kHz, 150 μJ, 1064 nm) for 5 min yielding ~150 mg/L gold nanoparticles. This suspension was diluted to a concentration of 10 mg/L. The subsequent laser fragmentation procedure was performed using the second harmonic of a Nd:YAG nanosecond laser (Innolas, Spitlight, 10 ns, 100 Hz, 75 mJ, 532 nm) for 4 h with a fluence of about 0.7–0.8 J/cm^2 without (pH 8) and with 10 wt% hydrogen peroxide (Fluka) in water (pH 5) and 0.6 mM NaOH (Applichem). The experiments were performed using the 4.5 mm raw beam in a glass vessel with 4 mL gold nanoparticle suspension.

2.2. Graphene nano sheets and adsorption of gold atom clusters to GNS

The graphene nano sheets were prepared by the reduction from oxidized graphite. This oxidized form of graphite was dispersed in water and reduced by hydrazine hydrate, resulting in graphene nano sheets as described from Siburian et al. [36]. The gold atom clusters used for this experiment were fabricated in 10 wt% hydrogen peroxide. Subsequently these gold clusters were adsorbed to the GNS under continuous treatment with a sonotrode and by heating of the cluster suspension to 80 °C. GNS fabrication and gold cluster adsorption were performed in the Faculty of Pure and Applied Sciences at the University of Tsukuba.

2.3. Particle analysis

Gold particle suspensions were characterized by UV/Vis-spectroscopy using a Cary 50 (Varian Inc.) spectrometer. TEM pictures were taken with a Zeiss EM190 microscope and a Jeol JEM-2100 high resolution transmission electron microscope (NIMS, Japan). Particle sizes were detected in an analytical disc centrifuge DC 24000 (CPS instruments) at 24 000 rpm and by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern).

3. Results and discussion

Here, we present a combination of laser ablation and oxidative fragmentation to generate ligand-free colloidal gold clusters. Laser fragmentation of gold nanoparticles in pure water results in a particle size reduction similar to experimental findings of Amendola et al. [31]. Size quenching and stabilizing effects for small amounts of salts are currently reported [37,38]. Here we combined the stabilizing effect of a small amount of sodium hydroxide (NaOH) with the oxidative potential from hydrogen peroxide (H_2O_2). Both additives are chosen since they offer the opportunity of a carbon-free stabilization of gold particles <4 nm. Addition of NaOH is not mandatory, but helpful to increase the pH of the solution for sufficient colloidal stability as the low pH resulting from the addition of H_2O_2 could cause destabilization of laser-generated colloidal gold particles. Nevertheless, all involved species are based on oxygen and hydrogen and no irreversible attachment of anions like chloride have to be considered. For applications where sodium might be harmful (e.g. specific catalytic reactions) the cation could be replaced by ammonium or other alkaline additives.

The corresponding UV/Vis spectra of the particle colloids after ablation and for fragmentation with 0.6 mM sodium hydroxide show a shift in plasmon resonance from 530 nm to 510 nm (Figure 1) which is equivalent to a particle size of around 40 nm and 6 nm respectively [39,40].

In contrast to this, the presence of hydrogen peroxide during the fragmentation process changed the particle size of the colloid without observing any precipitation. The significant decrease of plasmon resonance of the fragmentized particles might be explained by the fabrication of non-plasmonic particles [41] in both cases, with and without hydrogen peroxide. However, if hydrogen peroxide is present the particles size further decreases. This is observed by a plasmon resonance peak shift from 530 to 507 nm.

Figure 1 summarizes the influence of hydrogen peroxide on the particle size. Analysis was performed after laser ablation (black curve), fragmentation of particles in water with sodium hydroxide (red dashed curve) and after oxidative laser fragmentation in the presence of sodium hydroxide and hydrogen peroxide (blue dashed and dotted curve). Particle size distribution is determined from TEM images, which are exemplary shown on the bottom (a: after laser ablation, b: after pulsed laser fragmentation in water with low NaOH concentration (0.6 mM), c: after fragmentation in the presence of hydrogen peroxide (10 wt%) and 0.6 mM NaOH). The plasmon resonance shift and decrease of extinction in the UV/Vis-spectra correlate to the decrease of particle size after fragmentation which is also observed from TEM images.

This size reduction was confirmed by transmission electron microscopy (TEM) images and analysis in an analytical disc centrifuge (see also Figures S2–S4 and S7–S9). Gold nanoparticles generated by laser ablation without surfactants usually obtains particle diameter between 10 and 100 nm (Figure 1). Laser fragmentation reduces the size of these particles down to a mean size of 3.5 nm, for minute amounts of sodium hydroxide. TEM-analysis of particles fragmentized in the presence of both sodium hydroxide and hydrogen peroxide show product particles smaller than 3 nm whereas most particles are around 2.1 nm. These observations in the difference when hydrogen peroxide as oxidative reagent is present during the fragmentation process are statistically confirmed by particle size analysis using an analytical disc centrifugation, reported in Figure 2. This quantitative analysis confirms reduction of the particle size after the fragmentation and the positive effect of hydrogen peroxide for further particle size decrease. Therefore: (i) the educt gold nanoparticles are in a regime of tens of nanometers; (ii) laser fragmentation in water with 0.6 mM sodium hydroxide results in a hydrodynamic particle diameter of around 10 nm; (iii) the presence of hydrogen peroxide yields around 4–6 nm particles. Deviations of TEM histograms and the results from the analytical disc centrifuge might be explained by the measurement method. Sizes observed in the TEM correspond to a real particle diameter whereas particle sizes resulting by analytical disc centrifugation are enhanced by contributions of soft agglomerates and solvation shell.

Figure 3 (right) shows a zoomed gold cluster from a HR-TEM image with a measured lattice spacing of 0.2 nm (illustrated as black lines and arrows) which correspond to gold {2 0 0} planes in