Supporting Information

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Photoluminescence of Fully Inorganic Colloidal Gold Nanocluster and Their Manipulation Using Surface Charge Effects

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Section I: Laser-based synthesis of ligand-free Au NCs

LFL leads to a colloid containing plasmonic and proto-plasmonic particles. A detailed description of the laser-based fragmentation can be found in the following references. In brief, the interaction of nanoparticles with a high-intensity laser pulse leads to a temperature increase within the particles and the medium, causing phase transitions leading to phase explosion and fragmentation. The efficiency of laser fragmentation measured by the average product particle diameter and mass yield of particles smaller than 3 nm increases with increasing laser intensity. In recent in situ investigations, we could shed light on the phase-explosion mechanism during fragmentation and the subsequent ripening. This secondary particle growth after LFL is favored as it will reduce the specific surface area, which is thermodynamically driven as it results in a decreased free Gibbs enthalpy. To avoid particle growth, a stabilization strategy is required, which could be i) dilution to increase the mean free path length and thereby decrease the collision rate or ii) addition of electrostatic stabilizers which can 'shield' the particles by electrostatic repulsion and increase the Debye length. Note that the addition of organic ligands would also reduce secondary particle growth by steric stabilization. However, the omission of organic ligands is a central point in this work. In previous work, we have already demonstrated that the yield of Au NCs can be synergistically increased when LFL takes place in the presence of the two electrostatic stabilizers NaOH and NaCl. However, as this procedure does not guarantee a 100 % yield of particles smaller than 3 nm, and we observe an optical signal of larger, plasmonic particles (Figure S1A) 50 kDa centrifugal filters were used to separate remaining plasmonic particles. The separation was successful (Figure S1C) and no more plasmonic particles could be detected in the absorbance measurements (Figure S1B).
Figure S 1: A) Absorbance spectra after LFL of AuNPs with 0.3 mM NaOH and 0.3 mM NaCl B) Size distribution of Au NCs after LFL and subsequent filtration with 50 kDa centrifugal filter. The filtrate contains particle sizes between 0.4 – 4 nm. C) Corresponding absorbance spectrum.

Further size separation was conducted by using smaller MWCO centrifugal filters (10, 3, 1 kDa). Using 3 kDa filter, we were able to produce ultra-small particles (Figure 1B), which could be additionally analysed using ESI-MS. While the size distribution is given in Figure 1B of the main manuscript, additional information on this method can be found in the following section.

Figure S2: Nano ESI mass spectra of Au NCs in water recorded in negative mode. The red number assignment (at the red vertical lines) corresponds to charge states of the MW=7900 Da.
Figure S3: Spectra corresponding to deconvoluted nano ESI mass spectra between the charges states 4 and 7, rescaled with the formula $D_{Nanoparticles} = \sqrt[3]{\frac{M_{w \text{ nanoparticles}}}{M_{Au + 30.89602}}}$. We are assuming spherical shape and face centered cubic crystal structure.\(^4\)

Figure S4: Deconvoluted nanoESI mass spectra of precursor NCs (orange) and of fragmented NCs (black). The precursors’ ions undergo collisions with argon in the collision cell device on
the MS instrument. The difference between fragments and parents corresponds to the evaporation of around seven gold atoms and one negative charge.

**Section II: Surface adsorbates effect**

The variation of the pH value forces a pronounced alteration of the gold surface charge density as it leads to protonation or deprotonation of surface adsorbates (OH/O⁻). Following Ohshima et al., the surface charge density can be described as a function of the zeta potential, a factor that can be determined experimentally (see experimental section of the main manuscript) and describes the electric charge in Coulomb per surface area. Based on this it is possible to calculate absolute values of negative surface charges by simply dividing the surface charge density by the elementary charge and subsequently multiplying it by the mean particle surface. The mean particle surface is calculated from the experimentally obtained particle size distribution shown in Figure 1B (green curve) in the main manuscript. A comparison with the charge quantity of the elementary charge finally results in the number of free charge carriers on the particle surface.

![Graph](https://example.com/graph.png)

**Figure S5** Correlation between total number of surface charges and the surface charge density, calculated for LFL generated NCs with a mean diameter of 2.1 nm.

In addition, the change of the pH value shows an influence on the emission. To determine this, different ionic strengths of NaOH and HCl were added. All raw data can be found in Figure S6. Note that adjusting the pH value in a range between pH 4 and 12 does not influence the particle diameter (Figure S7).
Figure S6: Absorbance and emission intensity of Au NCs after adjusting the pH value in the range of pH 3 to pH 12.

Figure S7: Hydrodynamic particle diameter distribution of Au NCs after adjusting the pH value with HCl or NaOH.

Additionally, we checked the photophysical long-term stability of the particle's emission at two different surface charge densities of -0.031 C/m² and -0.059 C/m², corresponding to a solution pH of 7 and 10, respectively. Size distributions of the corresponding particles are depicted in Figures S8 A and D. The size distribution evaluated by AUC is unchanged after photoexcitation and after 1 week of storage.

Even though we found no significant differences in the particles' size distributions at pH=7 and pH=10 small deviations occurred even though the particles were taken from the same synthesis batch. Here, we cannot discriminate whether these differences are due to an impact of the charge on particle size or whether the charge density affects the measurement. We
measured the particle size with the AUC, which detects the movement of a sedimentation front which is formed after radial acceleration of a sample rotor. The temporal displacement of the sedimentation front allows the determination of the sedimentation coefficient. The sedimentation distribution can be described by the Lamm equation and is a function of the particle size. However, the sedimentation behavior can be influenced by charging effects.\[7\] Surface charges can act as a counterforce to sedimentation\[7\] so that particles could be perceived as smaller, as observed at pH=10. However, these slight differences do not impede the consecutive evaluation of particle stability.

Figures S8 B and E show the emission behavior measured at different times, and Figures S8 C and F show a summary of the emission intensity measured at 350 nm. Following this, the emission intensity changed neither for particles with 1 negative charge per particle (\(-0.031 \text{ C/m}^2\)) nor for particles with doubled negative surface charges per particle (\(-0.059 \text{ C/m}^2\)). Based on this, we conclude that the photophysical properties of fully inorganic gold nanoclusters are long-term stable."

**Figure S8:** Investigation of the photophysical stability at different surface charges. A-C) surface charge adjusted to \(-0.031 \text{ C/m}^2\), D-F) surface charge adjusted to \(-0.059 \text{ C/m}^2\). A) and D) particle size distribution of the particles measured before and after photoexcitation and storage for 7 days. B) and E) Emission spectra recorded after different times. C) and F) Emission intensity at 350 nm in correlation with storage time. Note that the emission intensity for particles increases with higher surface charge density (see also Figure 2 in the manuscript)
Section III: Additional information on the theoretical calculations

In the following, we will provide the details on the theoretical calculations carried out on the Au$_{38}$(OH)$_{24}$ gold nanocluster and the subsequently deprotonated species.

Analysis of excited states from SCIS

Figure S 9: Single-particle energies calculated with BHLYP/dhf-SVP-2c/COSMO(water) including spin-orbit coupling.
Table S 1: Analysis of excited states according to the SCIS results. The values in parenthesis after the single-particle excitations represent the contribution of a given single-particle excitation to a given excited state in percent.

| Excited state number | Energy [eV] | Transition dipole moment [a.u.] | Composition |
|----------------------|-------------|---------------------------------|-------------|
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO+2 (66%) |
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO (14%) |
| Total charge: 0      |             |                                 |             |
| 32                   | 4.24653     | $3.56 \times 10^{-1}$           | HOMO-2 $\rightarrow$ LUMO+2 (66%) |
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO (14%) |
| Total charge: -2     |             |                                 |             |
| 32                   | 4.28637     | $4.29 \times 10^{-1}$           | HOMO-2 $\rightarrow$ LUMO+2 (52%) |
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO (24%) |
| Total charge: -4     |             |                                 |             |
| 32                   | 4.37497     | $3.53 \times 10^{-1}$           | HOMO-2 $\rightarrow$ LUMO+1 (44%) |
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO+2 (18%) |
|                      |             |                                 | HOMO-1 $\rightarrow$ LUMO+2 (18%) |
| 36                   | 4.41981     | $1.04 \times 10^{-1}$           | HOMO-2 $\rightarrow$ LUMO+2 (66%) |
|                      |             |                                 | HOMO-2 $\rightarrow$ LUMO+1 (44%) |
Figure S10: Electron densities of the valence states for three different charge states calculated with wB97X-d/dhfsSVP-2c and the COSMO model with parameters for water.
Figure S 11: Electron densities of the conduction states calculated for different charge states calculated with wB97X-d/dhf-SVP-2c and the COSMO model with parameters for water.
Section IV: Structural resolution

Figure S12: Single-particle measurement of the observed crystal planes in HR-TEM measurements. The crystal structure is determined by a single particle fast Fourier transformation on the HR-TEM images in Figure S13 after measuring 60 individual particles. The x-error corresponds to the histogram Δd and amounts to 0.2 nm.

Figure S13: Representative HR-TEM images of Au NCs after LFL and ultracentrifugation using 50 kDa centrifugal filters.
**Figure S14:** A) HR-TEM image and B) corresponding Fast Fourier Transform. A crystal twinning is observed on the particle. The particle shows reticular planes consistent with the [011] zone axis. C) Observed cubic crystal structure (gold, Fm-3m) and D) corresponding reciprocal lattice.
Section V: Size effect on the photoluminescence behaviour

Figure S 15: Emission detected for surface dominated Au NCs after excitation with different wavelengths. Corresponding particle size distributions can be found in Figure 1 of the main manuscript.
Figure S 16: Emission detected for core-dominated Au NCs after excitation with different wavelengths. Corresponding particle size distributions can be found in Figure 1 of the main manuscript.
X-ray absorption and fluorescence spectra are corrected for background with polynomial functions in the Athena software of the ifeffit package. The oscillatory EXAFS information $\chi(k)$ as a function of electron momentum $k$ was derived by subtracting a spline-fitted step function at the L(III) edge. A spectrum of a gold foil in transmission and the large colloids together with the pure $\chi(k)$ function are shown in Figure. S14. The EXAFS data were analysed by Fourier transforming the modulation in absorption $\chi(k)$ with a $k^2$ weight in the range of $k = 1.5$ and 15 Å$^{-1}$.

Reference samples for the XANES analysis were 2 mM aqueous HAuCl$_4$ (Chempur) in 3-valent state with chloride nearest neighbors, 2mM aqueous HAuCl$_4$ (Chempur) in 100 mM cetyl trimethyl ammonium bromide (CTAB, Chempur) reduced by 2 mM sodium ascorbate (Roth chemicals) in 1-valent state with bromide neighbors.$^{[9,10]}$

![Figure S17](image)

**Figure S17:** Normalized X-ray absorption of the small and large particles as a function of X-ray energy (left) and $k^2$ weighted EXAFS oscillations as a function of electron momentum $k$ (right).

**Section VI: Emission lifetime of core dominated Au NCs**

We measured the lifetime of 1.1 nm fully inorganic gold nanocluster with the particle size distribution presented in Figure S18 A. Here, we focused our lifetime measurements on the most stable and most reproducibly found emission at 340 nm (core emission). The summarized lifetimes can be found in Table S2.
**Figure S18:** Determination of the lifetime of fully inorganic NCs: A) Size distributions of the measured Au NC. B) Fluorescence spectrum. C) Time-resolved decay of the fluorescence measured at 340 nm.

**Table S2:** Summary of measured lifetimes $\tau_i$ and fractional intensities $I_i$ after tri-exponential fitting of the decay curves in Figure S18C

| Emission centered at | $\tau_1 (I_1)$ | $\tau_2 (I_2)$ | $\tau_3 (I_3)$ |
|----------------------|----------------|----------------|----------------|
| 340 nm               | 2.20 ± 0.01 ns (60.5%) | 1.01 ± 0.01 ns (36.1%) | 0.09 ± 0.01 ns (3.4%) |

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