

Direct observation of photo-mechanical stiffness in alkanethiol-capped gold nanoparticles supracrystals by ultrafast small-angle electron diffraction

Giulia F. Mancini^{1,2}, Francesco Pennacchio³, Tatiana Latychevskaia⁴, Javier Reguera⁵, Francesco Stellacci⁶ and Fabrizio Carbone³

¹Laboratory for Ultrafast Spectroscopy, Lausanne Center for Ultrafast Science (LACUS), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

²Paul Scherrer Institut, WSLA/210, 5232 PSI Villigen, Switzerland

³Laboratory for Ultrafast Microscopy and Electron Scattering, Lausanne Center for Ultrafast Science (LACUS), Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

⁴Physics Institute, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

⁵CIC biomaGUNE, Paseo de Miramón 182C, 20009 Donostia-San Sebastian, Spain. Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain.

⁶Supramolecular Nanomaterials and Interfaces Laboratory, Institute of Materials, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

Abstract: We demonstrate that ultrastiff bonding between nanoparticles can be engineered by ad hoc assemblies of ligands, reaching strengths comparable to that of strong covalent bonds. Our observation relies on femtosecond small-angle electron diffraction.

1. Introduction

Ligand-coated nanoparticles (NPs) can form two-dimensional supracrystals with mechanical and electronic properties relevant for a wide range of applications [1]. Recently, ultrafast small-angle electron diffraction has enabled to resolve both their static ordering properties and their photo-induced motions [2-4] with combined femtosecond (fs) temporal and Ångströms (Å) spatial resolution. With this technique, light pulses can be used to set the supracrystals out of equilibrium. The transfer of energy from the electronic excitation to the underlying structural degrees of freedom leads to motions of both the NPs and the ligands that can be monitored by diffracting ultrashort electron pulses.

In this work, we show that the Debye-Waller effect can dramatically vary in supracrystals coated by ligand chains with a different number of carbon atoms. Specifically, our observations reveal that local stiffness can be created in an octanethiol-capped nanoparticles supracrystal by Van der Waals forces to an extent comparable to stiff solids characterized by strong homonuclear covalent bonding. Moreover, our simulations demonstrate the presence of a direct correlation between the degree of order of the NPs within grains of the supracrystal and its local (nearest-neighbor) mechanical stiffness.

2. Experimental Methods

In our experiment (Fig. 1a, inset), the driving laser is a KMLabs Wyvern centered at a wavelength of 780nm, with 0.65mJ pulse energy, 50fs pulse duration, at a repetition rate of 20kHz. The temporal chirp of the photoemitted electron bunches (30keV) is compensated by a radiofrequency cavity operating in the TM₀₁₀ mode [4, 5], yielding ~300fs/160µm bunches at the sample, each containing up to 6×10⁵ electrons. The collected diffraction patterns are formed on a phosphor screen and detected on an intensified electronic imaging camera capable of single electron detection with an array of 1300×1340 pixels (side length of 20µm), and single binned on-chip at 1MHz pixel readout rate. The experiments were conducted in transmission geometry at room temperature, with 500 accumulations with 300 gates per exposure for every time delay. Photoinduced changes in the samples were initiated by 1.5eV pump-pulses focused to a spot of 220µm. The absorbed fluence was 100µJ/cm² [6]. Gold nanoparticles capped with 1-octanethiol (C8), 1-decanethiol (C12), or 1-octanedecanethiol (C18) were synthesized using a modification [7] of the method described by Zheng et al. [8], and transferred after synthesis an amorphous carbon-coated grid through a Langmuir-Schaefer deposition. All experiments were conducted with consistent parameters for all three samples.

3. Results and Discussion

We analyze the light-induced decay of the intensity of the diffraction feature $I(s)$ associated to the local (nearest to next-nearest neighbor) hexagonal arrangement of the gold NPs in each supracrystal (Fig. 1b). In Fig. 1a each intensity trace was normalized to the average value at negative times ($t < t_0$) and fitted to a mono-exponential curve (solid lines). Photoinduced thermal disorder in the NPs hexagonal arrangement is evidenced in both samples by the transient decrease of $I(s_1)$. Remarkably, the $I(s_1)$ decay time-scale for C8, $\tau = 2.6 \pm 0.3$ ps, is significantly shorter than the one for C12, $\tau = 12.1 \pm 0.9$ ps. The C8 supracrystal (pink circles) shows a decay in diffracted intensity comparable to graphite (purple triangles) [9], suggesting a strong coupling of the electronic and lattice degrees of freedom. When the ligand length increases (C12, blue triangles) the system is characterized by a softer electron-phonon coupling, similar to soft metals such as Bismuth (blue squares) [9].

* Corresponding author: [Lausanne, Switzerland](mailto:giulia.mancini@epfl.ch).

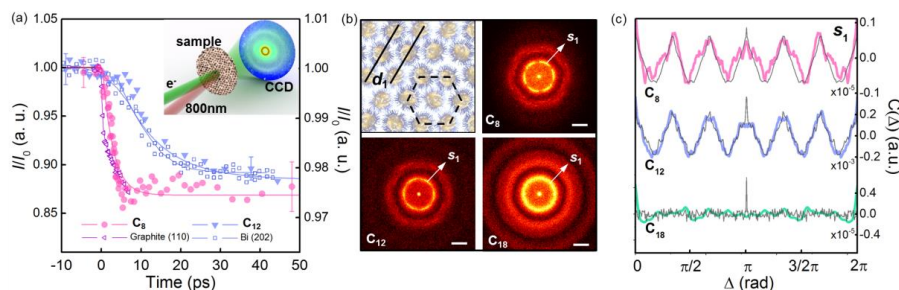


Fig. 1. (a) Ligand length-dependent dynamic response of C8 and C12 supracrystals upon photoexcitation, compared to the time-response of graphite and Bismuth [9] in UED transmission experiments. Inset: Ultrafast small-angle electron scattering experimental layout. (b) Schematic illustration of a two-dimensional monolayer of alkanethiol-functionalized NPs with NPs arranged in a hexagonal lattice with crystallographic planes distance d_1 , and FT simulation from the TEM images of each sample. (c) The CCF for each sample (C8 pink, C12 blue, C18 green) at $s_1=2\pi/d_1$, from small-angle UED experiments, is compared to the ones obtained at s_1 from the corresponding FT simulation (grey overlay).

In alkanethiol-capped NPs supracrystals the presence of attractive Van der Waals interactions among ligands holds the NPs in the supracrystal together via interdigitation [10]. The comparable rapidity in the suppression of the diffracted intensity for C8 suggests that in this supracrystal the interdigitation of the shorter ligands provides a very efficient channel for transferring energy between the initial electronic excitation to structural motions of the NPs. The velocity of the $I(s_1)$ suppression is directly related to the coupling strength between the electronic and structural degrees of freedom in each supracrystal, which significantly differs with the ligand length.

We demonstrate for each sample the presence of a direct correlation between the observed Debye-Waller decay, and the symmetry of the NPs within the supracrystal grains. We explore ligand length-dependent order-disorder correlations considering the squared amplitude of the Fourier Transform (FT) of the Transmission Electron Microscopy (TEM) images from each supracrystal (Fig. 1b). The agreement between the angular cross-correlation functions [2] at s_1 for experiment and FT simulations (Fig. 1c) suggests the presence of a recognizable translational symmetry of the NPs distribution within single domains for the C8 and C12 samples, where an $I(s_1)$ suppression upon photo-excitation is retrieved. In C18, where no local symmetry is found, the randomized distribution of the scattering objects within each domain leads to the presence of a liquid-like phase, where no correlation between transient changes and NPs arrangement can be unraveled.

4. Conclusions

We reported that local mechanical stiffness can be created in supramolecular assemblies by Van der Waals forces to an extent comparable to systems characterized by strong covalent bonding with ultrafast small-angle electron diffraction. By showing the direct correlation between the observed Debye-Waller decay, and the arrangement of the NPs within the supracrystal grains, our simulations support that the local symmetry of the NPs plays a role in the short-range degree of coupling between the electronic and lattice degrees of freedom.

5. Acknowledgements

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6. References

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