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Modeling of laser-assisted nanoparticle fragmentation, sintering, and alloying

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https://doi.org/10.1016/j.mtbio.2019.100033

Motivation

Tailoring optical properties: medical applications, imaging, photo-acoustics, photonics, etc.



Optical properties of multilayer-polyelectrolyte films with incorporated gold nanomaterials (solid nanoparticles and hollow nanoshells) R. W. Day, Materials Science (2009)





From tunable core-shell nanoparticles to plasmonic drawbridges: Active control of nanoparticle optical properties Chad P. Byers et al. *Science Advances* 04 Vol. 1, no. 1 (2015)

Au Nanomatryoshkas as Efficient Near-Infrared Photothermal Transducers for Cancer Treatment: Benchmarking against Nanoshells, Ciceron Ayala-Orozco et al., ACS Nano 8(6) (2014)

Motivation

Tailoring magneto-optical properties for medical applications, imaging, water-splitting, etc.



Evolution of the Magnetic and Optical Properties in CocoreAushell and (CoRh)coreAushell Core–Shell Nanoparticles, Junais Habeeb Mokkath *The Journal of Physical Chemistry C*, (2017)



Polymerization time

A general strategy to synthesize chemically and topologically anisotropic Janus particles Jun-Bing Fan, *Science Advances* 21, Vol. 3, no. 6 (2017)

Why Lasers ?



- 1. Green synthesis methods, bio-compatibility
- 2. Easy control over NP properties
- 3. Scaling-up possibilities
- 4. Possibility to create stable ultra-structures



Mechanism of pulse laser interaction with colloidal nanoparticles A. Pyatenko et al., Laser&Phot. Rev. 2013

Laser is a versatile tool that can be used for

- formation of nanoparticles

 in vacuum
 in gas
 in liquid
 in a solid
- modification of nanoparticles fragmentation –tailoring of sizes sintering – can create nanohybrides and nanocomposites, thus tailoring their optical,

magnetic, and acoustic properties

Laser –induced modifications of nanoparticles are promissing for many applications in photonics, medicine, optics, etc.

Typical experiments



Pulsed laser interactions in vacuum and in a gas phase



Laser-induced ablation/fragmentation in liquids



Laser-assisted multi-functional nanohybrids fabrication in liquids: see talks by Zhaneta Swiatkowska and by Anton Popov et al. at SECAM 2021



Vincenzo Amendola, Padova, Italy

https://doi.org/10.1002/cphc.202100021 Kinetically Stable Nonequilibrium Gold-Cobalt Alloy Nanoparticles with Magnetic and Plasmonic Properties

The mechanisms involved are still not enough understood... How modeling can help?

Laser Interactions with NPs



SINGLE NANOPARTICLES heating, melting, structural transformations, evaporation, fragmentation

Laser Interaction with NPs in Liquids

Classical Modeling



 C_e, C_{NP}, C_m - heat capacities; k_e, k_{NP}, k_m - thermal conductivities; T_e, T_{NP}, T_m - temperatures; $\vec{J} \cdot \vec{E}$ - Joule heating source (absorption); γ_{ei}, h - energy transfer rates; ρ_{NP}, ρ_m - ion densities.



Advantages: rather easy equations, estimations of temperatures Limitations: hard to account for electron ejection/injection, etc..

Ultra-Short Laser Interaction with NPs

Non-Equilibrium Electron Sub-system

Conduction band (free) electrons model

Boltzmann equation

intra/inter

$$\frac{\partial f(E)}{\partial t} = \left(\frac{\partial f(E)}{\partial t}\right)_{e-e} + \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} + \left(\frac{\partial f(E)}{\partial t}\right)_{intra/inter}$$

 $\cong \frac{P_{abs(t)}}{K} [f(E-\hbar\omega) - 2f(E) + f(E+\hbar\omega)]$

$$E_{max} = E_F + \varphi$$

Terms for e-e, e-ph scattering & absorption

$$\left(\frac{\partial f(E)}{\partial t}\right)_{e-e} \cong \frac{f(0)C_{ee}}{\sqrt{E}} \frac{\partial}{\partial E} \left[f(E)\left(1-f(E)\right) + k_B T_e \frac{\partial f}{\partial E}\right]$$

$$\left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} \cong \frac{C_{ep}}{\sqrt{E}} \frac{\partial}{\partial E} \left[f(E) \left(1 - f(E)\right) + k_B T_i \frac{\partial f}{\partial E} \right]$$

$$k_B T_e = \frac{1}{f(0)} \int_0^{E_{max}} f(E) \left(1 - f(E)\right) dE$$

$$\rho_{NP}C_{NP}\frac{\partial T_{NP}}{\partial t} = -A \int_{0}^{E_{max}} \left(\frac{\partial f(E)}{\partial t}\right)_{e-ph} E^{3/2} dE$$

Here, we can transit back to spatial TTM model to add spatial thermal diffusion etc.





Laser Interaction with NPs in Liquids

Interaction regimes and mechanisms involved



Electron emission

Au : N_{therm} is the total number of emissible electrons emissible : $N_{therm} = \alpha . n_{\epsilon}$

where n_{ϵ} is a number of electrons with kinetic energy that exceeds the work function per atom at an electron temperature of T_{e}

 $n_{\epsilon} = \int_{\epsilon}^{\infty} EDOS(E) \cdot f(E, \mu(T_{e}), T_{e}) \cdot dE$

electronic density of states for a broad range of T_e chemical potential value depends on T_e

Criteria of fissility, also called Rayleigh instability factor

if X > 1, where

 $X = (N_{therm}^{2}/N_{e}) / (16.\pi r_{ws}^{3}.\sigma/e^{2}) =>$

Particle explosion can occur

 $\alpha = 4V / a_{fcc}^{3}$ total number of atoms in the particle

Calculated absorbed fluence, fluence needed for boiling/evaporation (red), for melting (magenta) and for electrostatic decomposition (blue)



Calculated threshold fluence

150 fs @400 nm



Resonant particles can be decomposed electrostatically... However, smaller and larger particles are expected to be fragmented due to classical thermal-mechanical effects.

Ultra-short Laser interaction with a single Au NP in vacuum

Classical Molecular Dynamics (MD) simulations:

Decomposition of the ablated material after the absorption of laser radiation

and nanoparticle fragmentation



T. E. Itina, L. V. Zhigilei, B. J. Garrison The Journal of Physical Chemistry B 106 (2), 303-310 (2002)

Ultra-short Laser interaction with a single Au NP in vacuum



Ultra-short Laser interaction with a single Au NP in liquid



MD simulations

Heating during e-ph coupling

Larger particle – longer heating and cooling, higher thresholds

30 nm radius gold particle in water absorbing laser pulse of **150 fs** at **400 nm** with laser fluence of **12.3 mJ/cm²** Gaussian time profile

> L. Delfour and T.E. Itina J. Phys. Chem. C 119 (24), 13893 (2015)

NB: Liquid or matrix participate in NP cooling down affects the final configuration

DOUBLE NANOPARTICLES AND NANOHYBRIDS melting, sintering, mixing, core-shells and Janus nanoparticles

Optical properties of nanohybrids

(a) (b) 50 nm 10 nm (C) $(d^{2.0})$ core-satellite Au-Fe NPs Au NPs Fe oxide NPs 1.5 500 Extinction (a.u.) 004 Sounts 300 300 50 nm Au satellites 200 x10 0.5 Fe oxide cores 100 -0 0.0 L 300 20 40 50 60 70 80 400 500 600 700 800 900 0 10 30 Diameter (nm) Wavelength (nm)

see talk by Anton Popov et al. CECAM 2021



Au NPs with radius in the range [10-100] nm





Gold dimers in water



If both particles have the same size

Larger inter particle distance => more pics

=> shift towards blue

Inter-particle distance remains constant

Larger particles => more pics => shift towards blue

Absorption depends on size, composition, separation, etc...

Bi-Metallic Nanoparticles and Aggregates: MD simulations



General Trends in Core–Shell Preferences for Bimetallic Nanoparticles

Namsoon Eom, Maria E Messing, Jonas Johansson, and Knut Deppert*



Read Online





Ultra-short Laser-induced NP sintering, Janus NPs



T.E. Itina at al.

Ultra-short Laser-induced NP sintering, Janus NPs

AuNP +AuNP, different sizes



Figure 9. Snapshots of cross-sections of two Au nanoparticles with $d_{p,0}=3$ (gray) and 4 nm (white) undergoing sintering at T = 800 K at t = 0, 0.01, 0.1, 1, 10, and 30 ns.

Ultra-short Laser-induced NP mixing (Nanoalloy formation)

MD simulations

R1, R2~10 unit boxes

Similar sizes the same T, but different materials Co and Au











- Simulation starts from a Janus configuration
- Then both particles are heated to the same temperature
- Then, the system is cooled down back to room temperature

Mixing seems to be easier when both particles have comparable sizes and temperatures

mixed

Ultra-short Laser-induced NP hybrid (core-shell) formation



- Simulation starts
 from a Janus
 configuration
- Then both particles are heated to different temperatures
- Then, the system is cooled down back to room temperature

When one particle is larger and this particle is more absorbing, partial Janus configuration or an almost core-shell one is observed 26

T.E. Itina at al.

Ultra-short Laser-induced NP hybrid (core-shell) formation



Different materials: Fe and Au Different sizes The same temperatures

Time-evolution of potential energy



FeNP 1700+AuNP 1700

N_t







- Simulation starts from a Janus configuration
- Then both particles are heated to the same temperature
- Then, the system is cooled down back to room temperature

Core-shells can be also formed when one particle is larger, but both particles are heated to the same T

Ultra-fast heating and cooling of alloy NP







SUMMARY

- 1. Laser is a very powerful and versatile tool suitable not only for the control over nanoparticle sizes but also for a wide range of manipulations with nano objects involving processes such as melting, reshaping, sintering, mixing, etc.
- 2. The involved processes are often non-equilibrium and therefore are still hard to be generalized.
- 3. Several modeling examples of the processes involved have been demonstrated revealing the role of size, temperature, and composition of nanoparticles, as well as the heating and cooling conditions.

Thank you very much!