Bachelor’s Degree in Engineering Physics

Higher Technical School of Engineering Physics

Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure

Analysis and Discussion of a Scientific Article

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1. Introduction

The article *"Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure"*, written by Rossi, Erhart, and Kuisma and published in *ACS Nano* in 2020, addresses a key topic in nanophotonics: the generation of hot carriers in metallic nanoparticles (NPs) via localized plasmons. This phenomenon, involving light absorption and its conversion into high-energy electrons and holes, has potential applications in areas such as photocatalysis, solar energy conversion, and optical sensing. The article specifically highlights how atomic-scale structural features of NPs influence the energy and spatial distribution of the hot carriers.

The relevance of this work lies in its ability to connect nanotechnology and quantum physics through simulations based on time-dependent density functional theory (TDDFT). This approach overcomes the limitations of experimental models, providing deep insight into atomic-scale processes that impact the efficiency of optoelectronic devices. In the context of the concepts studied in class—such as surface plasmon resonance and carrier dynamics—this article not only complements theoretical foundations but also explores practical implications.

The choice of this article is justified not only by its relevance in the field of nanophotonics, but also due to the high impact factor of *ACS Nano* (¿15) and the recognition of its authors within the scientific community. Since its publication four years ago, it has been cited 121 times, reflecting its impact and relevance in ongoing research.

2. Description

The article *"Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure"*, written by Rossi, Erhart, and Kuisma and published in *ACS Nano* (2020), addresses one of the most relevant phenomena in modern nanophotonics: hot-carrier generation in metallic nanoparticles (NPs) through the excitation of localized surface plasmons (LSPRs). This research emphasizes how the local atomic structure of nanoparticles directly affects the efficiency and distribution of these hot carriers, underlining the importance of structural design in advanced optoelectronic applications.

2.1. Key Concepts and Context

Localized surface plasmons (LSPRs) are collective oscillations of free electrons at a metal's surface, excited when light hits metallic nanoparticles at a specific frequency. As explained in **Topic 3.1**, this phenomenon allows light confinement below the diffraction limit, generating intense electric fields near the nanoparticles' surfaces. These plasmons can decay into high-energy electrons and holes—known as hot carriers—that have multiple applications in areas such as photocatalysis, molecular detection, and energy conversion.

The main challenge in this field is understanding how structural and morphological properties of nanoparticles influence hot-carrier generation and distribution. While previous studies relied on simplified models, this article uses detailed atomistic simulations to explore how specific surface sites (edges, corners, facets) contribute to carrier generation.

2.2. Methodology Used

The study's methodology is based on first-principles simulations using time-dependent density functional theory (TDDFT), an advanced technique for modeling the dynamic behavior of electrons under optical fields.

The authors considered silver nanoparticles with icosahedral geometries that exhibit well-defined plasmonic resonances. To excite the plasmons, a monochromatic Gaussian-type light pulse was applied, described by:

$$v_{\text{pulse}}(t) = E_0 \cos(\omega_0(t - t_0))e^{-(t-t_0)^2/2\tau_0^2},$$

where:

- E_0: Amplitude of the applied electric field.
- ω_0: Pulse frequency, tuned to the plasmonic resonance ($\omega_0 = 3.6\,\text{eV}$).
- τ_0: Pulse duration (3 femtoseconds).
- t_0: Central time of the pulse.

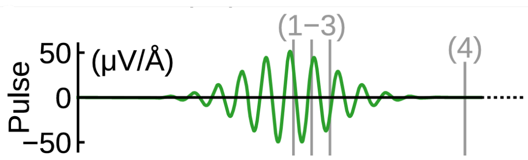

Figure 1: Electric field pulse applied to the nanoparticle, with frequency tuned to the plasmonic resonance. Adapted from Rossi et al., ACS Nano, 2020.

The system's dynamic behavior was studied by solving the electronic motion equations and analyzing the spatial and energy distributions of the generated carriers.

2.3. Main Results

The study reveals several key findings:

1. **Importance of Surface Sites:** Sites with low atomic coordination—such as corners, edges, and {100} facets—show significantly higher hot-carrier generation compared to central sites or highly coordinated {111} facets. This is due to the more inhomogeneous electronic densities at surface sites, which increases excitation probabilities.

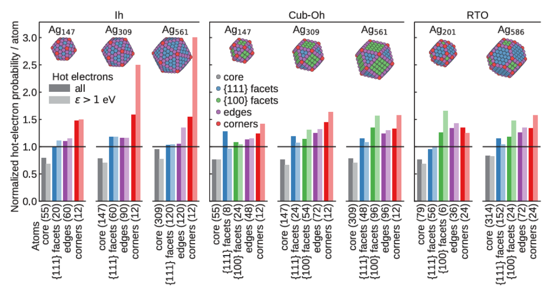

Figure 2: Spatial distributions of hot carriers in silver nanoparticles with different geometries: icosahedral (Ih), cuboctahedral (Cub-Oh), and truncated octahedral (RTO). Lower-coordination sites show higher hot-electron generation, as highlighted by color. Adapted from Rossi et al., ACS Nano, 2020.

As shown in Figure 2, low-coordination surface sites such as corners and edges exhibit higher hot-carrier generation. This contrasts with inner regions or {111} facets, which contribute less due to higher atomic coordination.

2. **Energy Redistribution:** After the initial plasmon excitation, the damping (dephasing) process redistributes energy into electron-hole transitions ($i \rightarrow a$), defined by:

$$\Delta E(t) = \sum_{i,a} \omega_{ia} P_{ia}(t),$$

where ω_{ia} is the transition energy between states i and a, and $P_{ia}(t)$ is the transition probability over time.

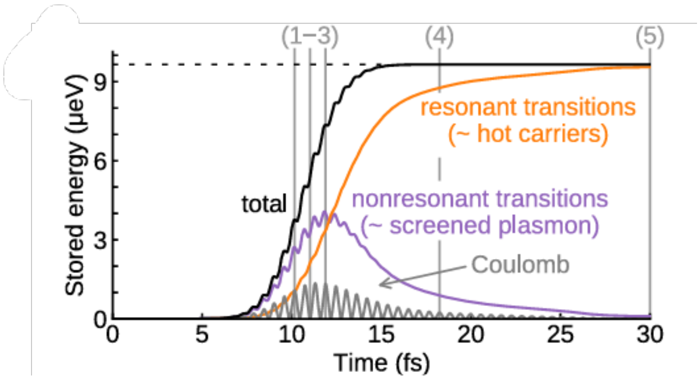

Figure 3: Temporal evolution of the energy stored in the excited electronic system. Absorbed energy (black line) is redistributed into resonant (orange) and non-resonant (purple) transitions after plasmon damping. Adapted from Rossi et al., ACS Nano, 2020.

3. **Spatial Distributions:** Hot electrons are concentrated predominantly at the nanoparticles' surface sites, while central sites contribute minimally. This result highlights the importance of structural design for maximizing efficiency in practical applications.

2.4. *Relation to Class Topics*

This work is directly connected to multiple topics from the course:

- In **Topic 3.1**, we explored the physics of surface plasmons and their ability to confine light in metallic nanoparticles—a core concept to understand the excitation described in this article.

- **Topic 3.6** discussed how the optical properties of nanomaterials can be tuned by structural design. This principle is central to the article, which shows how specific nanoparticle sites influence hot-carrier generation.

- In **Topic 3.7**, we studied nonlinear optical processes such as plasmon damping, which are directly related to energy redistribution among carriers.

2.5. *Implications and Applications*

The results have significant implications for the design of nanophotonic and optoelectronic devices. By controlling the atomic structure of nanoparticles, hot-carrier generation can be optimized for applications such as:

- **Photocatalysis:** Enhancing chemical reactions via light.
- **Solar energy conversion:** Improving efficiency in solar cells based on metallic nanoparticles.
- **Optical sensors:** Precise molecular detection using hot-carrier-based spectroscopy.

2.6. *Partial Conclusion*

In summary, this article provides a deep perspective on how surface plasmons and local atomic structure influence the generation and distribution of hot carriers. By connecting theoretical concepts with practical applications, it lays a solid foundation for future research in nanophotonics and nanotechnology.

3. Personal Commentary and Critique

The article *"Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure"* stands out for its innovative approach to analyzing hot-carrier generation in metallic nanoparticles from an atomistic perspective. This level of detail offers valuable insights for designing more efficient nanodevices in applications like photocatalysis, solar energy conversion, and optical sensing. However, while the study presents solid and well-supported results, there are aspects that could be improved or further explored.

3.1. *Strengths*

One of the article's most notable strengths is its use of TDDFT-based simulations. This approach offers a deep understanding of dynamic processes at the atomic level—something difficult to achieve with traditional experiments. Moreover, the authors clearly demonstrate the link between local atomic structure and hot-carrier generation, showing that low-coordination sites like corners and edges are key to optimizing efficiency.

The article is also well contextualized within nanophotonics. Its connection to practical applications makes it highly relevant, especially given the rising importance of sustainable technologies like solar energy conversion.

3.2. *Areas for Improvement*

Although the theoretical approach is robust, a potential weakness is the lack of direct experimental validation. While the results are supported by advanced simulations, including experimental data would strengthen the conclusions even further. For example, comparing predicted hot-carrier distributions with real-time measurements using transient absorption spectroscopy could help validate their applicability.

Additionally, while several nanoparticle geometries are studied, it would be interesting to explore how other metallic materials or hybrid compounds, such as doped semiconductors, affect hot-carrier generation. This would open up new possibilities for custom material design based on specific applications.

3.3. Future Perspectives

The study opens a promising path for optimizing nanoparticle design for technological applications. In the future, it would be interesting to investigate:

- Integration of optimized nanoparticles into real devices, such as next-generation solar cells or ultrasensitive sensors.
- The influence of thermal effects and recombination processes on hot-carrier efficiency, as these may limit practical use.
- Development of fabrication strategies to design nanoparticles with specific geometries and atomic structures at an industrial scale.

Overall, the article not only contributes significantly to nanophotonics but also highlights the importance of atomistic design in modern nanotechnology. If the mentioned improvements are addressed and new geometries and materials explored, this research field could transform multiple industries—from energy to biomedicine.

4. Conclusions

The article provides a significant contribution to understanding dynamic processes in metallic nanoparticles. Through detailed simulations based on time-dependent density functional theory (TDDFT), the authors demonstrate how local atomic structure directly influences hot-carrier generation and distribution, emphasizing the importance of low-coordination sites like corners, edges, and {100} facets.

This work strongly connects theory with practical applications, opening new possibilities in fields such as photocatalysis, solar energy conversion, and optical sensing. The results show that atomic-scale structural design is not merely theoretical but a key tool for optimizing the efficiency of nanoparticle-based devices.

On a personal level, the article expanded my understanding of the underlying mechanisms in nanophotonics, particularly in relation to localized surface plasmons—a topic we explored deeply in **Topic 3.1**. It also reinforced the relevance of concepts studied in **Topic 3.6**, such as the influence of geometry and atomic structure on the optical properties of nanomaterials.

Finally, this work highlights promising prospects in the field. If combined with experimental advances and scalable fabrication strategies, the findings described could transform key industries such as energy, biomedicine, and sensing. This article not only reflects the state of the art in hot-carrier research but also sets a solid foundation for future exploration in nanotechnology and nanophotonics.

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