

Modeling of Light-Driven Heterogeneous Catalysis and Other Excited-State Processes at the Nanoscale

Background. Mitigation of greenhouse gas emission and energy security are the primary motivations to augment traditional carbon-based energy sources with renewables. Thus, the ever-increasing drive to use solar power in order to generate renewable electricity, fuel, and other useful chemicals has resulted in a surge in studies on photo-driven processes for light-harvesting materials. This includes photo-induced chemical reactions and charge-carrier generation and transport in semiconductors and metals. The need for better models and therefore greater understanding of reactions and processes involving electronically excited states, in conjunction with chemical reactivity, would be essential to further drive this research forward.

Research niche and expertise. Many great theoretical and computational groups have tackled, in various forms, the “materials-for-solar-energy” niche. I believe that my graduate training in solid-state physics and surface science at the University of Pennsylvania and my exposure to wavefunction methods and chemical catalysis at Princeton University have provided me a unique combination of tools and know-how to accurately explore, model, and understand the intricacies of the behavior of surfaces, as well as the ground- and excited-state chemical dynamics on surfaces and other interfaces. My combined training in both worlds (solid-state and chemistry) has prepared me to tackle the complexity of interaction of light and matter in the context of chemical reactivity and charge transport. Thus, my group will aim to develop the ability to model the chemistry and physics of interfacial phenomena, explicitly and carefully considering excited electronic states, which is a current scarcity in the field.

Goals. The goal of my future research is to use state-of-the-art computational tools in fields where the understanding of light-matter interactions and excited-state physics at the atomic-scale deliver practical design principles to accelerate the fabrication of useful, solar-driven technologies and applications. My group’s research areas of expertise will include (i) **visible light-driven photocatalysis**, and (ii) **nanoscale photovoltaics and charge-carrier transport across interfaces**. To explicitly model light-activated processes, it is crucial to perform accurate quantum mechanical calculations. Therefore, (iii) **a density-functional-theory (DFT)-based quantum mechanical partitioning and embedding method will be developed and tested for covalent semiconductors**, which would allow for formally exact many-body but expensive quantum mechanical calculations to be conducted.

Summary of proposed work. My near-term research endeavors cover three topics sharing the theme of **nanotechnology for energy**. **Figure 1** summarizes the workflow in optimizing materials for catalytic and solar applications. Each stage will involve different level(s) of theory to maximize discovery rate, balanced with appropriate accuracy. Combinatorial searches and structural

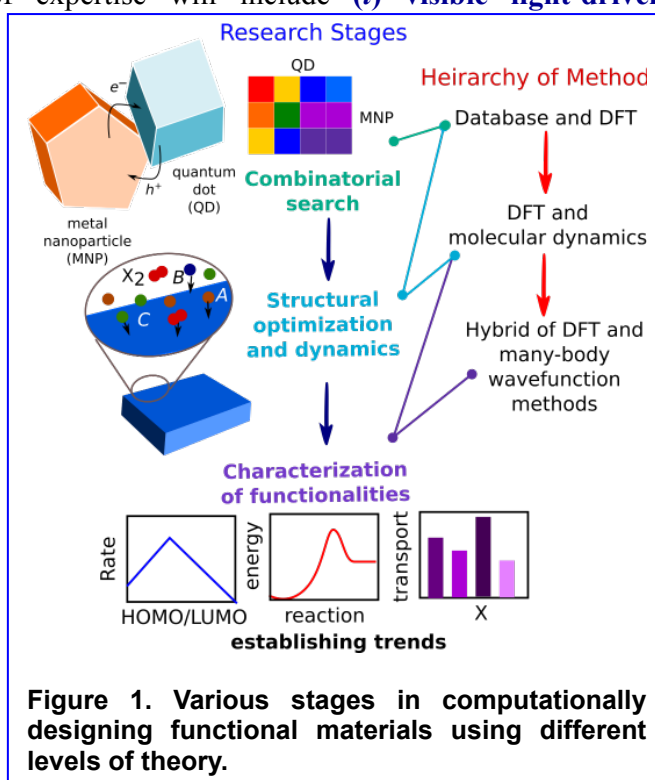


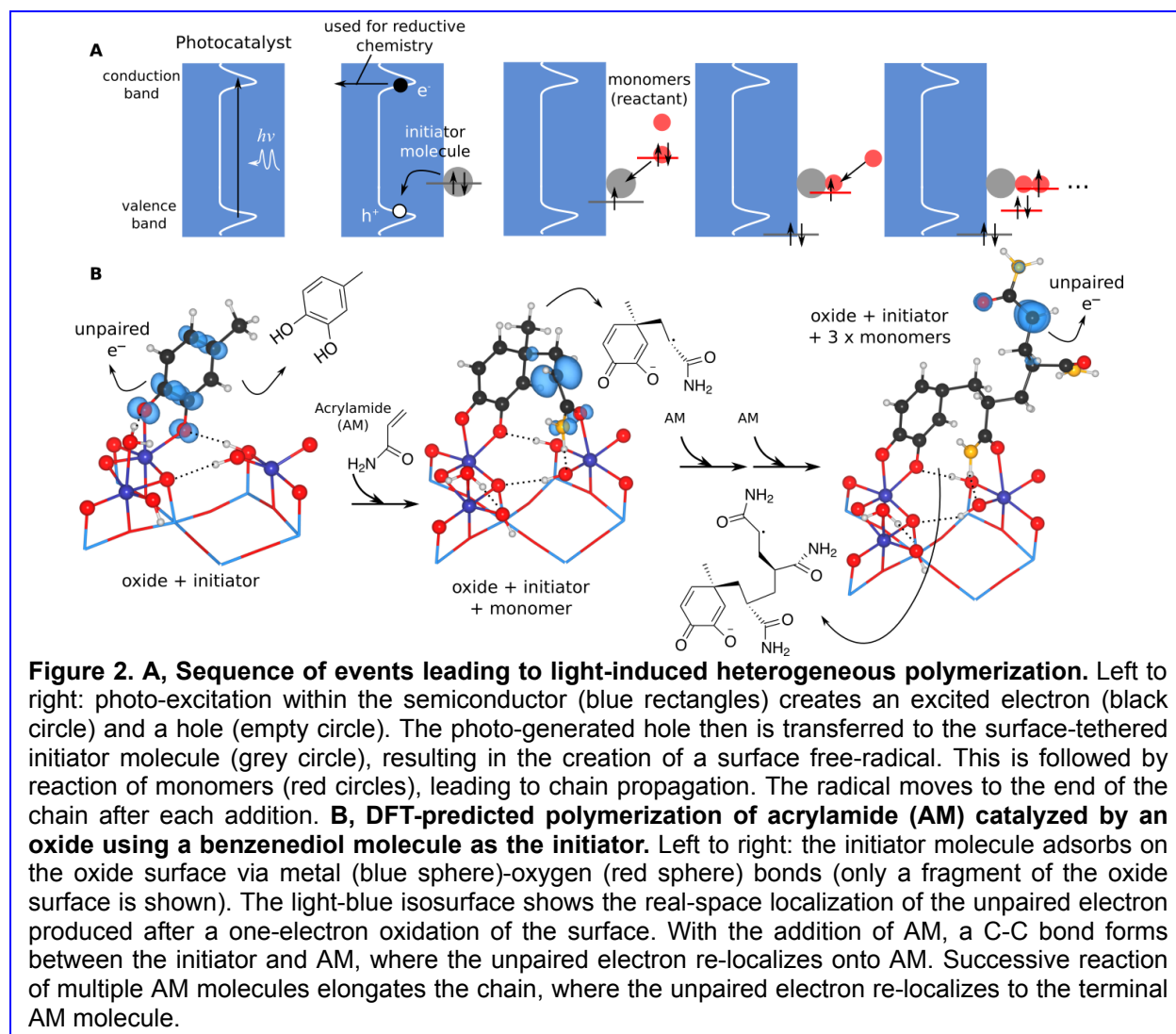
Figure 1. Various stages in computationally designing functional materials using different levels of theory.

discovery will be explored through **database mining**, augmented with quantum mechanical **DFT** simulations. Desirable functionalities will be identified and quantified **through DFT and formally exact many-body wavefunction methods**. Through the latter calculations, figures of merit will be established and trends may be discerned to guide future searches. Experimental collaborations will be key in all of these stages. Experimental input will be included to guide the search or verify the veracity of the generated data and established trends.

I. Visible-light-driven photocatalysis on semiconductors

This project will explore the possibility of directly using light-generated, energetic charge carriers in semiconductors to catalyze reactions, with emphasis on organic chemistry reactions, *e.g.*, free-radical polymerization to synthesize mass-resolved “designer” polymers.

Background and focus. Semiconductors generate energetic charge carriers (electron and holes) upon illumination with light. These charge carriers are chemically active species that could potentially catalyze chemical reactions on the surface of the semiconductor, but are subject to the constraint of their lifetimes: electrons and holes may recombine or are “trapped”, and in the process lose their energies in the form of heat or reemitted light. This project thus will focus on finding ways to stabilize these charge carriers on the surface so that they may be used to catalyze the important



chemical reactions in agricultural, pharmaceutical, manufacturing, and energy industries. These include polymerization chemistry, C-H bond activation, and water splitting, to name a few. Application in polymerization chemistry is described below as an example.

Free-radical polymerization. Azo compounds and inorganic/organic peroxides are typically used to initiate free radical polymerization.¹ The free radical is generated via thermal decomposition or photolysis of the unstable initiator molecules, which require special handling and low-temperature storage. Traditional radical polymerization schemes suffer from inefficient initiation, due to slow radical generation. These schemes are also known to generate polymers with uncontrolled molar mass, and subsequently broad mass distributions, due to rapid radical recombination and disproportionation.² I therefore propose to explore an alternative avenue to generate radical species for polymerization via light-induced decomposition of molecules on photoactive semiconductors (e.g., TiO₂, MoS₂, and GaP), whereby they are generated *in situ* and may remain immobilized on the surface. **Figure 2A** shows schematically the sequence events after electron-hole pair generation in a semiconductor (panel 1), which oxidizes a generic electron-donor molecule forming a free-radical (panel 2). The surface-oxidized molecule (initiator) then catalyzes the polymerization process while still attached to the surface (panels 3 to 5). The main potential advantages of this scheme are (i) the radicals are surface bound and thus free-radical recombination processes are avoided, and (ii) unstable molecules need not be used as initiators (free radicals are generated “on the fly” using light).

Proposed work. Searching for a molecule with the right band alignment of a given semiconductor or *vice versa* is a challenge. For a surface radical to form *in situ*, it is imperative to have an effective charge separation between the surface-tethered molecule (the initiator) and the semiconductor. For example, the molecule must have its highest occupied molecular orbital (HOMO) above the valence band of the semiconductor to facilitate electron transfer from the molecule to the semiconductor. This specification relieves the requirement that the molecule be chromophoric. Semiconductor-to-molecule hole-transfer has been experimentally demonstrated when simple oxygenated organics, e.g., aldehydes,³ ketones,³ and alcohols,⁴ are adsorbed on TiO₂ and exposed to ultraviolet (UV) light. From preliminary calculations, **Figure 2B** illustrates the DFT-predicted polymerization of acrylamide (AM), heterogeneously catalyzed on a metal-oxide surface with a benzenediol initiator.⁵ The reactions shown are found to be favorable after the one-electron oxidation of the surface-bound benzenediol. The unpaired electron localizes on the initiator molecule (free-radical), which leads to a cascade of AM reactions elongating the polymer chain. The unpaired electron re-localizes at the terminal AM after each addition.

Surveying different initiator molecule-semiconductor combinations from first-principles. A combination of periodic-DFT and accurate embedded correlated wavefunction (ECW) methods (via density functional embedding theory, or DFET⁶) will be employed to find suitable pairs of semiconductors and initiator molecules. Suitable semiconductors and molecules will be pre-screened using band gaps and absorption frequencies as respective metrics, from available databases. DFT then will be used to determine the relative alignment of the frontier electronic states of the semiconductor and of the molecule, while the exact description of the surface localized excitations (generation of surface electron-hole pairs) and their energies will be investigated by suitable excited-state theories. The latter include multi-configurational, post-Hartree-Fock methods such as complete active space self-consistent field (CASSCF),⁷ multi-reference singles and doubles configuration interaction (MRSDCI),⁸ and *n*-electron valence second- and third-order perturbation theories (NEVPT2/3).⁹ Performing excited-state methods will be possible via DFET despite the large total system size (see Section III). Reconstruction of the surfaces of the semiconductors,¹⁰⁻¹¹ and modifications of the functional groups available in the initiator molecule (*i.e.*, their effects on radical stabilization and relative band alignment), will also be explored via DFT-based methods to determine and optimize the components' interactions.

Primary expected outcomes. I aim to determine the physics governing stabilization of charge carriers

on surfaces of photoactive materials. This would help identify the necessary initiators and semiconductors and thus establish an extended library of reactions that may use light as a catalyst.

Funding opportunities. I will seek federal funding through the NSF: via the Catalysis (PD-17-1401) and CAT (PD-09-6884) grant programs, the AFOSR: via the Army Research Office Broad Agency Announcement for Basic and Applied Scientific Research (W911NF-17-S-0002) grant program, and the DOE: via the SunShot Catalyst prize (DE-FOA-0001126) grant program.

II. Tandem quantum dots and plasmonic nanoparticles for photovoltaics

This project aims to explore the possible synergistic combinations of quantum dots (QDs) (with tunable band gaps) and plasmonic metal nanoparticles (MNPs) (with tunable light-scattering and absorption properties) for photovoltaics and possibly catalysis.

Background and focus. Tandem photovoltaics maximize harvesting of light by combining complementary properties of different photo-active materials. For example, large- and small-band-gap semiconductors can be combined such that a wider range of energy of the solar spectrum can be utilized simultaneously and more efficiently. Another method is to combine *p*- and *n*-type doped semiconductors to facilitate electron-hole pair separation, which improves quantum efficiency. Here, I propose to study the physics and chemistry associated with combining plasmonic MNPs and semiconducting QDs, each having their own unique optical properties, to achieve highly efficient photovoltaic materials. The optical and electronic properties of materials dramatically change at the nanoscale, primarily via electron or electric-field confinement effects. High-scattering and low-absorption metals, *e.g.*, Cu, Ag, Au, and Al,¹² exhibit an enhanced optical response at the nanoscale. Local surface plasmon resonances (LSPRs) enable these MNPs a size- and shape-dependent, enhanced optical extinction response, with optical extinction cross-sections four to five orders of magnitude higher than most organic chromophores.¹³ For example, Au is known to have a size- and shape-tunable maximum LSPR from the UV to near infrared.¹³ QDs, on the other hand, are nanoscale semiconductors that exhibit size-dependent optical absorption. The degree of quantum confinement of the photo-generated electron and hole results in a tunable maximum absorption frequency of the material, with smaller particles exhibiting blue-shifted absorption frequencies. **Figure 3** shows the possible interaction between plasmonic MNPs and QDs. The MNP, exhibiting a high optical response, may act as an antenna to enhance absorption and therefore enhance electron and hole-pair generation within the QD. Since both components have a tunable frequency of the maximum optical response, an optimally tuned combination or combinations of MNPs and QDs can open doors for optically tunable photovoltaic devices with enhanced absorption profiles.

Proposed work. To be able to realize MNP-QD tandem photovoltaics, detailed quantum mechanical studies on the

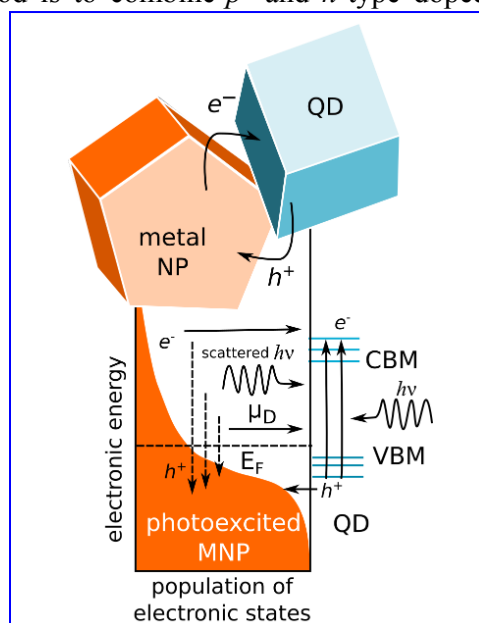


Figure 3. Electronic coupling in a tandem metal nanoparticle (MNP) and quantum dot (QD) system.

Both particles can be photo-excited, perturbing their electronic structures and creating electron-hole pairs. The conduction band minimum (CBM) and valence band maximum (VBM) of the QD are illustrated relative to the photo-excited MNP's Fermi level (E_F). Dipole-induced (μ_D) excitation within the semiconductor, due to plasmonic light scattering of the MNP and direct charge transfer between particles, are illustrated. Both processes can enhance charge-carrier generation.

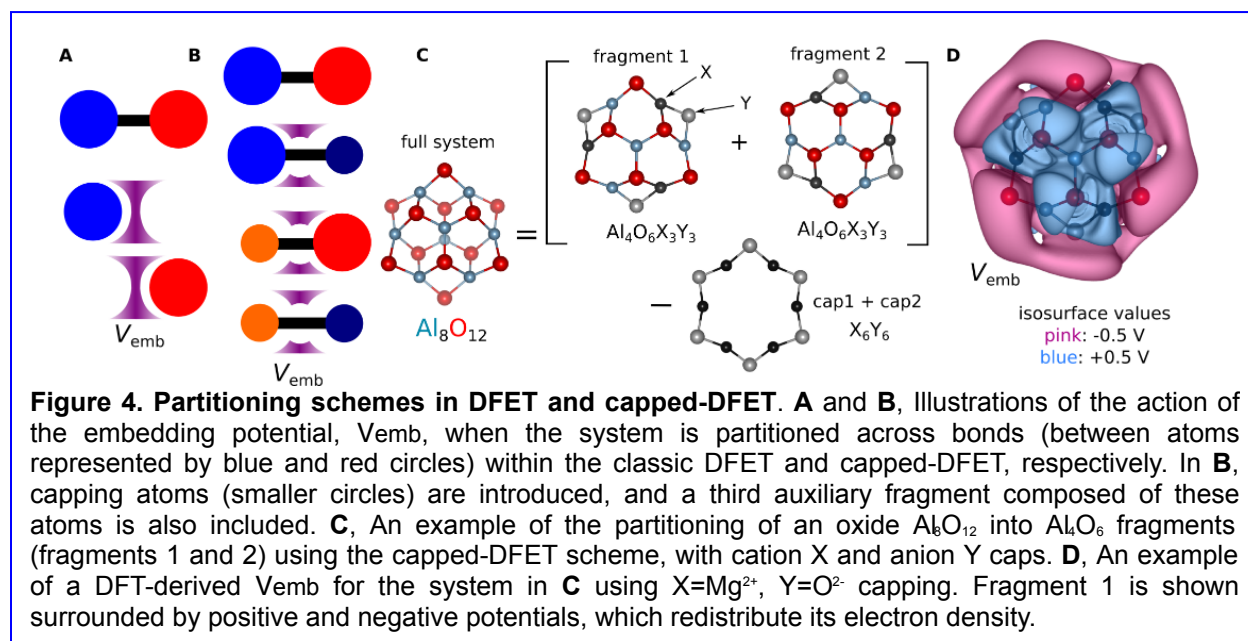
bulk properties of each individual component, as well as on their chemical and electronic couplings, are required. It is likely that the optical response of the composite material is more than just the sum of its individual components. A combinatorial search will be conducted based on the optical gap of the QD (experimental and generated DFT-based theoretical databases) and the light scattering properties of the MNP (also experimental and theoretical databases generated via electrodynamics simulations¹⁴ and DFT). Possible combinations include earth-abundant plasmonic metals such as Cu and Al, with widely available QDs such as CdSe, CdTe, and ZnS. The interface will play a key role in both charge-carrier transport and local exciton generation across the MNPs and QDs (**Figure 3**). Additionally, energy transfer via plasmon-induced resonance energy transfer (PI-RET)¹⁵ through electric dipole interactions between the photo-excited MNPs and QDs is also likely (**Figure 3**). DFT-based and accurate ECW methods will be employed to be able to model these phenomena accurately (see **Section III**).

Primary expected outcome. This project will create the phenomenological foundation for coupling QDs and plasmonic MNPs together as a single functional photoactive material.

Funding opportunities. I will seek federal funding for this project through the NSF, via the Energy for Sustainability (PD-17-7644) and Process Systems, Reaction Engineering and Molecular Thermodynamics (PD-17-1403) grant programs.

III. Capped density functional embedding theory for covalent systems

This project will further test and expand the implementation of a quantum mechanical partitioning method, DFET, to include extended covalent materials for photochemical and photovoltaic applications.



Background and focus. Systematically improvable CW methods are ideal for obtaining an accurate quantum mechanical description of chemical systems. These formally exact theories would be desirable when one needs to model excited-state properties, where DFT usually fails. The major drawback of these methods is the poor scaling of their computational cost with system size.¹⁶ To afford such computationally demanding calculations, the chemical system may be partitioned into a smaller fragment containing all of the chemically relevant parts (an active site), and a relatively unperturbed auxiliary fragment that acts as the environment of the former fragment. The active site

then may be described using more accurate methods in the presence of a potential (an electrostatic field) derived from a lower-level quantum mechanical method, *e.g.*, DFT, so that the smaller fragment may behave as if it belongs to a larger system. **Figure 4A** describes the classic partitioning method employed in DFET,⁶ where the embedding potential simulates bonding interactions that are otherwise absent in the individual fragments. One current limitation of this method is when partitioning of the system breaks highly directional covalent bonds, leading to unpaired electrons (radicals). To saturate these bonds, one may introduce capping atoms of complementary valence¹⁷⁻¹⁸ (referred to as link atoms in other schemes¹⁷). Shown in **Figure 4B** is the partitioning and atom-capping scheme across covalent bonds. However, the capping elements are not part of the full system, and therefore their contributions have to be removed from the energy- and electron-density representations. A third auxiliary fragment composed of the capping elements is illustrated, with contributions subtracted from the sum of the capped fragments. **Figure 4C** shows the implementation of capped DFET to an aluminum-oxide cluster. The embedding potential is optimized such that the sum of the electron densities of the capped fragments minus the density of the auxiliary fragment equals that of the full system (**Figure 4D**). The embedding potential, into which all of the fragments are embedded, effectively tunes the individual electronic Hamiltonians to simulate the full system.

Proposed work. [Benchmarking has to be established and limitations of this method defined to ensure successful and proper implementation.](#) The method will be tested both in a small cluster of inorganic transition-metal-based compounds and organic molecules. Properties such as light absorption energies and reaction energetics will be used as metrics for accuracy. The method will also be tested on covalent crystals, as well as their surfaces and interfaces, which would be essential in modeling heterogeneous catalysis and charge transport. [After successful implementation and testing, it will be used in both projects described in Sections I and II.](#)

Primary expected outcome. This project will establish a tool that will make possible the accurate prediction of electronically excited-state processes in photoactive and catalytically active materials for photochemical and photovoltaic applications.

Funding opportunities. I will seek federal funding for this project through the NSF, via the Condensed Matter and Materials Theory (NSF-16-596) and Computational and Data-Enabled Science and Engineering (PD-12-8084) grant programs.

References

1. Sheppard, C. S.; Kamath, V. R., *Polym. Eng. Sci.* **1979**, *19* (9), 597.
2. Colombani, D., *Prog. Polym. Sci.* **1997**, *22* (8), 1649.
3. Henderson, M. A.; Deskins, N. A.; Zehr, R. T.; Dupuis, M., *J. Catal.* **2011**, *279* (1), 205.
4. Shen, M. M.; Henderson, M. A., *J. Phys. Chem. Lett.* **2011**, *2* (21), 2707.
5. Martirez, J. M. P.; Rappe, A. M., *in preparation* **2017**.
6. Huang, C.; Pavone, M.; Carter, E. A., *J. Chem. Phys.* **2011**, *134* (15), 154110.
7. Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M., *Chem. Phys.* **1980**, *48* (2), 157.
8. Roos, B. O.; Siegbahn, P. E. M., *Int. J. Quantum. Chem.* **1980**, *17* (3), 485.
9. Angeli, C.; Cimraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J. P., *J. Chem. Phys.* **2001**, *114* (23), 10252.
10. Morales, E. H.; Martirez, J. M. P.; Saidi, W. A.; Rappe, A. M.; Bonnell, D. A., *ACS Nano* **2014**, *8* (5), 4465.
11. Martirez, J. M. P.; Kim, S.; Morales, E. H.; Diroll, B. T.; Cargnello, M.; Gordon, T. R.; Murray, C. B.; Bonnell, D. A.; Rappe, A. M., *J. Am. Chem. Soc.* **2015**, *137* (8), 2939.
12. Blaber, M. G.; Arnold, M. D.; Ford, M. J., *J. Phys.-Condens. Matter* **2010**, *22* (14), 143201.
13. Jain, P. K.; Lee, K. S.; El-Sayed, I. H.; El-Sayed, M. A., *J. Phys. Chem. B* **2006**, *110* (14), 7238.
14. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C., *J. Phys. Chem. B* **2003**, *107* (3), 668.
15. Li, J. T.; Cushing, S. K.; Meng, F. K.; Senty, T. R.; Bristow, A. D.; Wu, N. Q., *Nat. Photonics* **2015**, *9* (9), 601.
16. Dieterich, J. M.; Carter, E. A., *Nat. Rev. Chem.* **2017**, *1* (4), 0032.
17. Chung, L. W.; Sameera, W. M. C.; Ramozzi, R.; Page, A. J.; Hatanaka, M.; Petrova, G. P.; Harris, T. V.; Li, X.; Ke, Z. F.; Liu, F. Y.; Li, H. B.; Ding, L. N.; Morokuma, K., *Chem. Rev.* **2015**, *115* (12), 5678.
18. Huang, C.; Munoz-Garcia, A. B.; Pavone, M., *J. Chem. Phys.* **2016**, *145* (24), 244103.