

## Atomistic Multiscale Simulation of Nanostructured Materials for Photonic Applications

Alexander Bagaturyants, Michael Alfimov

Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7a, build. 1, Moscow 119421  
Russia  
[sasha@photonics.ru](mailto:sasha@photonics.ru)

Nanotechnology is a new, just incipient field of science and engineering, in which substances are controlled at an atomic or molecular level. Because new substances with a prescribed atomic and molecular structure are created in nanotechnologies by means of controlled manipulation with atoms and molecules, the use of multiscale atomistic simulation methods is of fundamental necessity. Hierarchically constructed nanostructured materials, in which the structure of a lower level of scale is built into the structure of a higher level of scale, attract particular interest. The development of nanostructured materials for optical chemical gas sensors is an example of this application. The functionality of such a material is provided by a photoactive molecule (indicator molecule, IM) such that it strongly changes its optical response (mostly, luminescence) upon interaction with a target molecule (detected or analyte molecule, AM). IM represents the lowest level of the hierarchy and is built into a local structure forming a receptor center (RC), which in its turn is built into a nanoparticle (NP). An NP may bear many RCs. Finally, nanoparticles are assembled into a layer or a multilayered structure (nanoparticle assembly, NPA), which may have regular ordering, forming a photonic lattice.

The goal of simulation in this case is to predict the optical properties of the entire structure (sensory material) and its response to various AMs. Direct calculations in real time and space scales are impossible with the currently available computational resources. Instead, a multiscale approach is used, in which simulations and calculations at each level of scale are performed using methods and approximations appropriate for the corresponding scale, while the results of modeling the structure and properties of a material at a lower level are transferred as input data to the next, higher level of scale.

Modeling materials for the sensing layer of optical chemosensors is considered as an example of the general strategy of multiscale atomistic modeling of hierarchically constructed nanostructured materials for organic nanophotonics. The main steps of such modeling are considered: modeling at the molecular level, modeling at the supramolecular level, and modeling at the level of nanoparticles. Problems arising at each step of modeling are analyzed, and current approaches to their solution are discussed.

In our case of hierarchically constructed materials for optical chemosensors, the use of atomistic simulation methods is restricted to the first three levels: IM, RC, and NP. The description of the assembling (self-assembling) of NPs into the final NPA and the prediction of its optical properties and response require the use of continual or phenomenological approaches and is beyond the scope of this paper. Hence, the following levels and the corresponding problems will be considered:

- molecular level: methods and possibilities, molecular structure, absorption spectra, emission spectra, line shapes, radiative and nonradiative transition probabilities, Stokes shifts, and special cases of large Stokes shifts in organic molecules arising in so-called twisted internal charge transfer (TICT) states;
- supramolecular level: molecular complexes and complex-formation effects on absorption and emission spectra, the problem of correctly describing intermolecular interactions and the structure of supramolecular systems, corresponding methods and possibilities, interaction potentials and their construction, reactive potentials, molecular mechanics, quantum and classical molecular dynamics, Monte Carlo methods;
- nanoparticle level: formation and structure of nanoparticles, coarse-grained potentials and coarse-grained molecular dynamics, kinetic Monte Carlo techniques.

The possibilities of modern atomistic simulation methods are considered using specific examples:

- quantum-chemical or quantum-mechanical simulation methods as applied to relatively small atomic and molecular systems; without these methods, optical, electronic, mechanical, vibrational, chemical and other functional properties of a material cannot be predicted;
- simulation methods based on the use of classical force fields approximately describing the main features of quantum interactions among atoms in molecules and among molecules themselves (molecular mechanics and modern computational methods of statistical physics, such as molecular

dynamics and Monte Carlo methods); in the framework of classical force fields, one can describe the structure, thermodynamics, and dynamics of systems containing about 1000 and much more atoms.

- Methods taking into account solvation (polarization) effects using both continual and molecular models, which can be used to describe the structure of an AM chemisorbed on a NP.

Special attention is given to the problem of adequately describing intermolecular interactions, the problem of describing functional properties of main molecular or cluster components of a supramolecular system, the problem of conjugating different scales, and the problem of consistently describing the system, in particular, the problem of constructing classical potentials based on the results of quantum calculations, and the problem of describing the formation and growth of supramolecular systems.

## References

- [1] A.A. Bagatur'yants, A.Kh. Minushev, K.P. Novoselov, A.A. Safonov, S.Ya. Umanskii, A.S. Vladimirov, A. Korkin, In *Predictive Simulation of Semiconductor Processing Status and Chal-lenges*, Springer Series in Materials Science, Vol. 72, Dabrowski, J. and Weber, E.R. (Eds.), Springer Verlag, 2004, 295.
- [2] A.A. Bagatur'yants, M.A. Deminskii, A.A. Knizhnik, B.V. Potapkin, S.Ya. Umanskii, in *Thin Films and Nanostructures: Physico-Chemical Phenomena in Thin Films and at Solid Surfaces*, L. I. Trakhtenberg, S. H. Lin, O. J. Ilegbusi, eds., Elsevier (2007) 468.
- [3] A.A. Bagatur'yants, I.M. Iskandarova, A.A. Knizhnik, V.S. Mironov, B.V. Potapkin, A.M. Srivastava, T.J. Sommerer, *Phys. Rev. B* **78** (2008) 165125.
- [4] A.N. Vasil'ev, I.M. Iskandarova, A.V. Scherbinin, I.A. Markov, A.A. Bagatur'yants, B.V. Potapkin, A.M. Srivastava, J.S. Vartuli, S.J. Duclos, *J. Luminesc.* **129** (2009), 1555.
- [5] K.G. Vladimirova, A.Ya. Freidzon, O.V. Kotova, A.A. Vaschenko, L.S. Lepnev, A.A. Bagatur'yants, A.G. Vitukhnovskiy, N.F. Stepanov, M.V. Alfimov, *Inorg. Chem.*, (2009) 48 (23) 11123.
- [6] A.Ya. Freidzon, A.A. Bagatur'yants, E.N. Ushakov, S.P. Gromov, M.V. Alfimov, *Int. J. Quant. Chem.* **111**, (2011) 2649.
- [7] A.A. Safonov, E.A. Rykova, A.A. Bagatur'yants, V.A. Sazhnikov, M.V. Alfimov, *J. Mol. Mod.* **17** (2011) 1855.
- [8] V. Chashchikhin, E. Rykova, A. Bagatur'yants, *Phys. Chem. Chem. Phys.* **13** (2011) 1440.
- [9] M.V. Basilevsky, E.A. Nikitina, F.V. Grigoriev, A.A. Bagatur'yants, M.V. Alfimov, *Struct. Chem.* **22** (2011) 427.
- [10] A.Ya. Freidzon, A.V. Scherbinin, A.A. Bagatur'yants, M.V. Alfimov, *J. Phys. Chem. A*, **115** (2011) 4565.