Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education

1988	B.E. Kyoto University
1990	M.E. Kyoto University
1993	Ph.D. Kyoto University

Professional Employment

1993	Postdoctral Fellow, Institute for Fundamental Chemistry
1994	JSPS Postdoctoral Fellow
1994	Visiting Researcher, Heidelberg University (–1995)
1995	Assistant Professor, Kyoto University
2002	Associate Professor, Kyoto University
2006	Theoretical Research Division Supervisor, Kyoto University (–2008)
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009	APATCC Pople Medal
2009	QSCP Prize CMOA

Member

Assistant Professor
- ITO, Soichi

Post-Doctoral Fellow
- KOIZUMI, Ken-ichi
- ZHAO, Pei
- VIGNESH, K. R.

Visiting Scientist
- ZHAO, Xiang
- PRIYAKUMAR, Deva U
- BOBUATONG, Karan

Graduate Student
- KANAZAWA, Yuki
- SHIRAOGAWA, Takafumi

Secretary
- KAWAGUCHI, Ritsuko
- SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, "SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution," *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, "Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser," *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, "CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions," *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, "Cooperative H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Theoretical Study on the Optical Properties of Multichromophoric Systems Based on an Exciton Approach: Modification Guidelines1)

A degree of freedom of supramolecular and polymer design has been enhanced by recent advances in experimental techniques, where the design guidelines are demanded for developing optical materials. We propose post-modification strategy of emission and circularly polarized luminescence (CPL) of multichromophoric systems based on excitonic analysis. The strong decomposed CPL components originate from the interactions of exciton electric transition dipole moments between the chromophore and its adjacent monomers. The Frenkel-exciton decomposition analysis (FEDA) provides new possibilities for utilizing the potentials of multichromophoric systems.

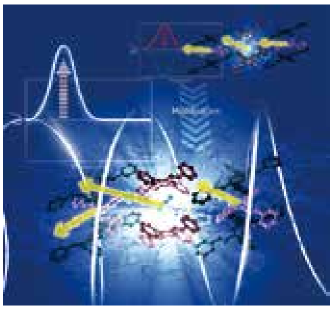

Figure 1. Post-modification strategy of emission and CPL of multichromophoric systems based on excitonic analysis.

2. Preferential Photoreaction in a Porous Crystal, Metal-Macrocycle Framework: Pd^{II} -Mediated Olefin Migration over [2+2] Cycloaddition2)

A nano-sized confined space with well-defined functional surfaces has great potential to control the efficiency and selectivity of catalytic reactions. In this work, we report that a 1,6-diene, which normally forms an intramolecular [2+2] cycloadduct under photo-irradiation, preferentially undergoes a photo-induced olefin migration in a porous crystal, metal–macrocycle framework (MMF), and alternatively [2+2] cycloaddition is completely inhibited in the confined space. A plausible reaction mechanism for olefin migration triggered by the photo-induced dissociation of the Pd–Cl bond is suggested based on UV-vis diffuse reflectance spectroscopy, single-crystal XRD, and MS-CASPT2 calculation. The substrate scope of the photo-induced olefin migration in MMF is also demonstrated.

3. Theoretical Insight into Configurational Selectivity of Functionalized Single-Walled Carbon Nanotubes Based on Clar Sextet Theory3)

Based on Clar's theory of the aromatic sextet, finite length models of single-walled carbon nanotubes (SWNTs) have been utilized to study the configurational selectivity of modified SWNTs via covalent functionalization with organic substitutions by density functional theory calculations. After considering near-armchair, near-zigzag, and zigzag SWNTs with distinct chiralities, it is found that the parameter R of semiconducting SWNTs plays a significant role in determining stability difference of functionalized SWNTs, *i.e.*, SWNTs with $R = 2$ exhibit better configurational selectivity than those with $R = 1$ when binding the same substituent to the sidewall of SWNTs.

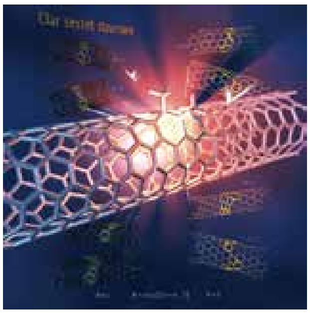

Figure 2. The configurational selectivity of modified SWNTs via covalent functionalization with organic substitutions to control the quantum dots.

4. Origin of Nb_2O_5 Lewis Acid Catalysis for Activation of Carboxylic Acids in the Presence of a Hard Base4)

The Nb_2O_5 surface catalyzes the amidation of carboxylic acids with amines via Nb^{5+} Lewis acid activation of the C=O group. In this work, DFT calculations were applied to theoretically investigate the C=O bond activation of a model carboxylic acid (acetic acid) on θ-Al_2O_3(110), anatase TiO_2 (101), and T-Nb_2O_5(100) surfaces. The position of the mean DOS of the *d*-conduction band of the active metal site relative to the Fermi energy level correlates well with the efficiency in the C=O bond activation and, consequently, the catalytic activity for amidation. Unlike a classical understanding of strong acid sites of metal oxide surfaces, interaction of a carbonyl HOMO with a metal unoccupied *d*-orbital, covalent-like interaction between a carbonyl group and metal adsorption site, is relevant to the present system.

References

1) T. Shiraogawa and M. Ehara, *ChemPhotoChem* **3**, 707–718 (2019). (Special Issue, Front Cover, Cover Profile)
2) H. Yonezawa, S. Tashiro, T. Shiraogawa, M. Ehara, R. Shimada, T. Ozawa and M. Shionoya, *J. Am. Chem. Soc.* **140**, 16610–16614 (2018).
3) P. Zhao, Y. Maeda and M. Ehara, *J. Phys Chem. C* **123**, 18629–18637 (2019). (Supplementary Cover)
4) P. Hirunsit, T. Toyao, S. M. A. H. Siddiki, K. Shimizu and M. Ehara, *ChemPhysChem* **19**, 2848–2857 (2018). (Front Cover, Cover Profile)

Award

SHIRAOGAWA, Takafumi; Best Poster Award, The 22nd Annual Meeting of Japan Society of Theoretical Chemistry.