Review Article

Artificial photosynthesis utilizing solid semiconductors and molecular metal complexes

1. Introduction

Since the establishment of SPring-8, researchers at Toyota Central R&D Labs. have extensively utilized it for the analysis of materials and devices for automotive technology, such as catalysts for exhaust gas purification and environmental cleanup, energy-storage batteries, and fuel cells. We express our sincere gratitude for this. Among these technical targets, this review highlights recent results on artificial photosynthesis, promoted as research ahead of time. This technology is expected to contribute to a sustainable society in the future, and the structural characteristics and dynamic behaviors of materials and devices obtained at SPring-8 and SACLA are valuable for progress in this research field.

Artificial photosynthesis is an uphill reaction technology that stores solar energy as chemical bond energy in small molecules by directly synthesizing organic compounds from carbon dioxide (CO_2) and water (H_2O) under mild conditions, such as a near ambient temperature and pressure under sunlight irradiation (Fig. 1). This technology involves a CO_2 reduction reaction (CO_2RR), which uses electrons and protons extracted from H_2O molecules via an oxidation reaction. We do not need to synthesize sugars as in natural photosynthesis, and prefer to obtain chemical raw materials, fuels, and other substances necessary for human society. To date, particulate photocatalysts, photoelectrodes, and photovoltaic (PV)-powered catalyst electrodes have been studied worldwide. However, CO_2 molecules are end products of the combustion of various organic compounds and are highly stable under ambient conditions, making it difficult to achieve a highly efficient CO_2RR.

Recently, however, our research group demonstrated that the solar-to-chemical energy conversion efficiencies have reached 4–20% at electrode scales ranging from 1 cm^2 to 1 m^2 for generating molecules smaller than sugars [1,2]. From the viewpoint of electrical energy conversion, the efficiencies of these systems exceeded 70%. Based on these demonstrations, novel visible-light-absorbing semiconductors, metal complex catalysts for the CO_2RR, and inorganic catalysts for water oxidation are required at the present stage. This review presents results obtained at SPring-8 BL33XU, BL47XU, as well as SACLA BL3 to understand the functions of these high-value materials in improving artificial photosynthetic systems.

2. Practical approach to artificial photosynthetic system for CO_2RR

Many studies have applied solid semiconductors or molecular metal complexes as photocatalysts under light irradiation in artificial photosynthetic systems. The catalytic reaction rate of these semiconductors can be enhanced by the surface loading of inorganic co-catalysts. The development of this technology relies on understanding the physical properties of individual materials for light absorption, charge separation, electron transfer, and catalytic reactions. Combining these materials without substantial energy loss is essential to achieving high conversion efficiency in the entire system. A new approach has recently emerged to realize solar-driven CO_2RR, that is, hybrid photosystems of solid semiconductors and molecular metal complex catalysts, which combine the functions of light absorption and charge separation of the semiconductors with the catalytic

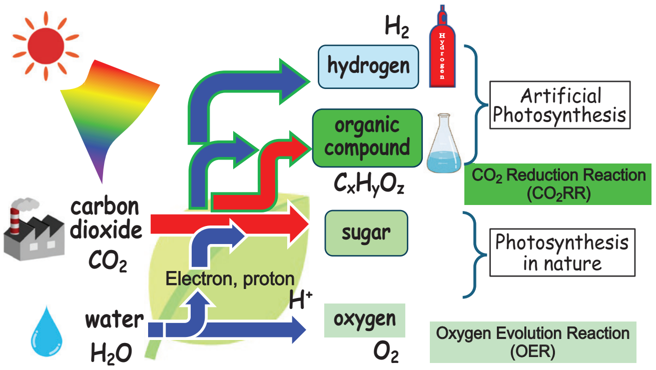

Fig. 1. Simplified schematic illustration of photosynthesis in plants and artificial photosynthesis. Conversion of CO_2 and H_2O to organic compounds under sunlight is the target.

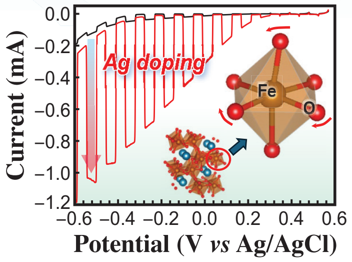

Fig. 2. Current–potential curves measured in O_2-saturated aqueous K_2SO_4 solution under chopped Xe-lamp light irradiation for Ag-doped $CaFe_2O_4$ photocathode. Inset shows crystal structure of $CaFe_2O_4$ and Fe–O octahedra.

functions of the metal complexes in a complementary manner. After demonstrating the high energy efficiencies and product selectivity mentioned in the introduction, the facilities and measurement technology at SPring-8 and SACLA are powerful tools for clarifying the structural and electronic aspects of new materials for application to artificial photosynthetic system platforms. The case studies are presented in this article.

3. Structural analyses of semiconductor and inorganic co-catalysts

The valence states of Cu and Ag co-catalysts for CO_2RR, supported on UV-responsive oxide semiconductor photocatalysts such as Nb_3O_8 nanosheets, particulate $SrTiO_3$:Al, Ga_2O_3, and $CaTiO_3$, have been investigated using X-ray absorption near edge structure (XANES) analysis at SPring-8 [3–5]. The local structure of the oxide semiconductor is also examined. This information supports our understanding of the photocatalytic reactions. Hybrid photosystems composed of semiconductors and molecular catalysts drive the CO_2RR with high efficiency under visible-light irradiation [6]. In $CaFe_2O_4$, which absorbs visible light with wavelengths shorter than 650 nm, Ag doping significantly enhances the photoelectrochemical reaction current. This improvement is attributed to the increased mobility of photoexcited carriers. Combined XANES analysis and Fourier transform of k^2-weighted extended X-ray absorption fine structure (FT-EXAFS), and X-ray diffraction (XRD) analyses suggested that the increased carrier mobility may originate from an improvement in the symmetry of the initially distorted Fe-centered octahedral coordination surrounded by six oxygen atoms in the orthorhombic crystal (Fig. 2) [7].

4. Band bending by angular-resolved HAXPES

In semiconductor photoelectrodes, band bending in the semiconductor, which extends from the bulk to the surface, is a critical factor for electron transfer from the semiconductor to the co-catalyst. Electronic interactions between the semiconductor surface and co-catalysts also play a vital role in determining the activity of the co-catalysts. Angular-resolved hard X-ray photoelectron spectroscopy (AR-HAXPES) is a valuable technique for investigating them by varying the take-off angle (θ_{toff}) of the detector.

Figure 3 displays AR-HAXPES spectra for the Ti $2p_{3/2}$ and Ta $3d_{5/2}$ core-state photoemissions of TiO_2 and N-doped Ta_2O_5 films, which exhibit n-type and p-type conduction, respectively [8]. N-Ta_2O_5 is the semiconductor used in the world's first demonstration of visible-light-driven photocatalytic CO_2RR in a hybrid photosystem [9]. The bare TiO_2 films exhibited similar spectral shapes at θ_{toff} of 65° (bulk phase; maximum analysis depth d of ~31 nm) and 10° (surface; d ~6 nm), with no significant shifts. However, the peak position of Ti $2p_{3/2}$ in bare TiO_2 (Fig. 3(a)) shifted negatively by 0.25 eV toward the surface upon loading a nanoscale Pt catalyst (Pt/TiO_2) (Fig. 3(b)). In contrast, for bare N-Ta_2O_5, the peak

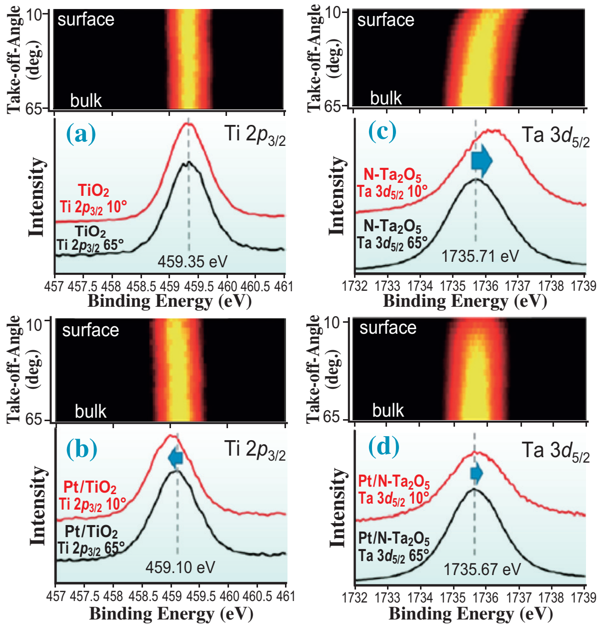

Fig.3. Series of Ti $2p_{3/2}$ spectra measured on **(a)** TiO_2 and **(b)** Pt/TiO_2 using angular-resolved HAXPES [θ_{toff}s 10° (red line) and 65° (black line)]. The upper panel represents a single shot of Ti $2p_{3/2}$ peaks from a 2D image for θ_{toff}s from 10° to 65°. Series of Ta $3d_{5/2}$ spectra measured on **(c)** N-Ta_2O_5 and **(d)** Pt/N-Ta_2O_5 by angular-resolved HAXPES (θ_{toff} of 10° and 65°). The upper panel is a single shot of Ta $3d_{5/2}$ peaks from a 2D image of θ_{toff}s from 10° to 65°. [8]

at θ_{toff} of 10° (surface; d ~5 nm) shifted by 0.40 eV toward a higher binding energy compared to that at θ_{toff} of 65° (bulk phase; d ~24 nm), indicating a significant downward band bending toward the surface (Fig. 3(c)). This 0.40 eV band bending was drastically reduced to 0.05 eV upon Pt surface loading (Fig. 3(d)), suggesting a stronger electrostatic interaction between Pt and N-Ta_2O_5. A similar trend was observed for metallic Rh and Au nanoparticles, and these interaction differences significantly affected the properties of the semiconductor photoelectrodes.

In contrast, surface linkages with molecular Ru and Re complex catalysts, in which metal ions are coordinated with bipyridine ligands, exhibited a minor effect on band bending [6]. These results indicate that the metal complexes have minimal influence on the electronic state of the semiconductor surface. However, an FT-IR spectroscopy investigation demonstrated that TiO_2 withdrew electrons from the Ru center of the complex at the CO_2RR site, whereas N-Ta_2O_5 did not. These results indicate that the CO_2RR activity at the Ru complex could be significantly altered when attached to TiO_2. These findings provide valuable insights into the design of nanoscale metal and metal complex catalysts for applications in semiconductor-based photosystems.

5. *Operando* XAS

A prominent trend in catalysis research is *operando* XAFS analysis, which allows for real-time analysis of catalysts under actual operating conditions, offering insights into their catalytic behavior. This requires specially designed reactors tailored to the physical form of the catalyst and specific operational parameters. These factors include the flow rates of the aqueous solution and gaseous CO_2, as well as the application of light and electrical energy. Once an optimized setup is established, *operando* XAFS serves as a powerful tool for investigating structural transformations during catalytic CO_2RR and the oxygen evolution reaction (OER) by water oxidation.

Our research demonstrated that the performance of electrocatalytic CO_2RR in aqueous solutions was significantly improved when using Mn, Co, and Re complex catalysts, which was attributed to the synergistic effect with K^+ and the carbon support. In particular, for the Co tetrapyridinoporphyrazine complex catalyst ([Co(PyPc)]), *operando* XANES confirmed that K^+ is essential for maintaining catalyst stability during operation, although detailed structural analysis was not possible due to the small amount of catalyst (Fig. 4) [10]. In a membrane electrode assembly (MEA) setup, the overpotential for CO_2RR was significantly reduced, enabling [Co(PyPc)] to effectively generate CO at an exceptionally low cell voltage of 1.9 V, achieving a reaction current density of 100 mA/cm^2. The turnover number, that is, the molar ratio of the produced CO to [Co(PyPc)], reached 3,800,000.

In another case study, *operando* XANES of a Br-bridged dinuclear Cu molecular electrocatalyst, facilitating the production of ethanol, ethylene, and propanol, confirmed the stability of the Cu(I) state during the CO_2RR [11].

The development of water-oxidation catalysts is also essential. Catalysts composed of earth-abundant elements are necessary to construct artificial photosynthesis systems in an environmentally sustainable manner. One example is an electrode composed of Ni-doped β-FeOOH(Cl) hyperfine nanorods coated with Fe-incorporated Ni hydroxide (β-FeOOH:Ni/Ni$(OH)_2$:Fe), with an average size of ϕ5 × 16 nm. The nanorods are synthesized at ambient temperature and normal pressure (β-FeOOH:Ni/Ni$(OH)_2$), and post-treatment at 200°C in KOH facilitates the diffusion of Fe and Ni between the core β-FeOOH:Ni and the surface amorphous Ni$(OH)_2$:Fe, resulting in a low overpotential for the electrochemical OER (Fig. 5(a)) [12]. *Operando* XANES and EXAFS were conducted in a CO_2-saturated pH 6.9 solution were conducted at the open-circuit potential (OC), where the OER did not occur. Along with XRD and Mössbauer spectroscopy, lattice distortion in the core β-FeOOH:Ni and the formation of short-range-ordered β-Ni$(OH)_2$:Fe were confirmed. Furthermore, under aqueous OER conditions (+1.6 V *vs* RHE), Fe *K*-edge spectra revealed a shortening of the Fe–Fe distance in the core β-FeOOH:Ni, while Ni *K*-edge spectra indicated a transition of short-range-ordered β-Ni$(OH)_2$:Fe toward β-NiOOH:Fe at the nanorod surface (Figs. 5(b,c)). The structural transformation was reversible and corresponded to an applied electrical bias. The dynamic change in structure responding to the electrical bias is a key factor in the enhanced OER activity compared to the as-synthesized β-FeOOH:Ni/Ni$(OH)_2$.

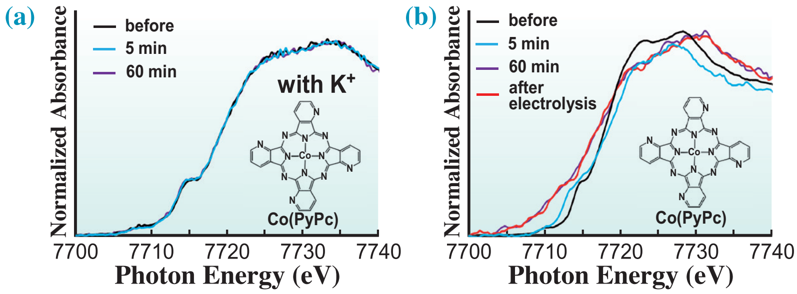

Fig. 4. *In situ* XANES spectra of molecular Co-catalyst with and without K salt. Spectra of (**a**) [Co(PyPc)] + K/carbon and (**b**) [Co(PyPc)]/carbon electrodes are measured at –1.4 V (*vs* Ag/AgCl) in CO_2-saturated aqueous solution [before electrolysis (black), 5-min electrolysis (blue), 60-min electrolysis (purple), and after electrolysis (red)].

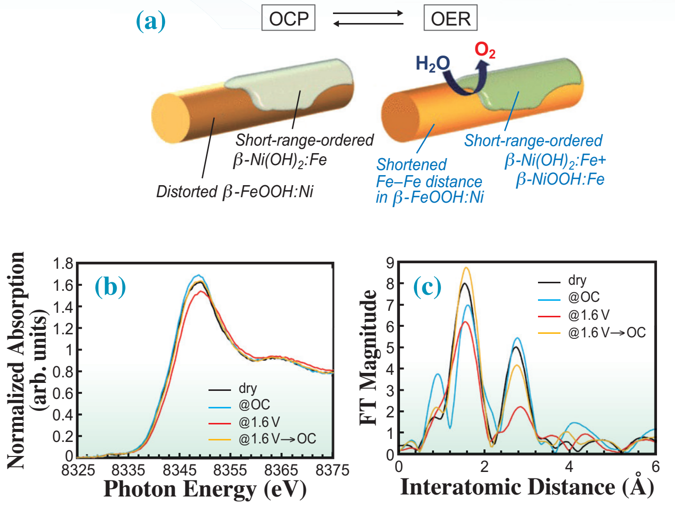

Fig. 5. *Operando* XAFS spectra acquired during the OER over the β-Fe/Ni electrode in aqueous KBB solution. **(a)** Ni *K*-edge XANES and **(b)** Ni *K*-edge EXAFS spectra. Conditions are (—) in air (dry), (—) in the solution without an electrical bias (OC), (—) in the solution under OER conditions of +1.6 V *vs* RHE, and (—) at OC after the OER.

6. Photoexcited electron transfer in an iridium complex photocatalysts measured at SACLA

Intersystem crossing (ISC) from the singlet excited state (^{1}MLCT) to the triplet excited state (^{3}MLCT) in photoexciton is a well-known ultrafast process. With the advancements in X-ray free electron lasers (XFELs), transient X-ray spectra can be recorded at a time resolution of less than 100 fs. Femtosecond time-resolved X-ray absorption near-edge structure (TR-XANES) spectroscopy was employed to investigate the visible-light excitation dynamics of mononuclear iridium(III) terpyridine (tpy) 2-phenylpyridine (ppy) ([Ir(tpy)(ppy)Cl]$^+$), a photocatalyst for CO_2RR. ISC was observed, revealing that the photoexcited MLCT had a lifetime of 114 fs. Theoretical calculations successfully reproduced the TR-XANES spectral changes in the molecule, directly capturing the rapid structural transformation around the Ir atom associated with ISC to the hot triplet state (Fig. 6). In contrast, subsequent relaxation to the lowest triplet state via internal conversion was not detected, suggesting that this process primarily occurs at ligands such as tpy rather than around the Ir center [13].

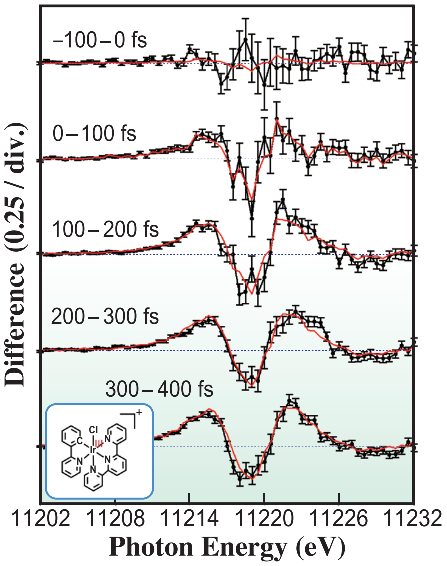

Fig. 6. Femtosecond TR-XANES spectra of [Ir(tpy)(ppy)Cl]$^+$ in acetonitrile.

7. Summary

Continuous research is necessary for artificial photosynthesis to reach a stage at which it can be regarded as a practical technology for future energy carrier production and environmental conservation. To this end, the analyses of key component materials related to light absorption, charge separation, catalytic functions, and their combinations at SPring-8 and SACLA are indispensable. Furthermore, expanding the application of these techniques and developing new methodologies for measurements under device conditions are anticipated.

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