## 2-2-8. Photochemistry of Semiconductors

### Overview

Semiconductor photochemistry has advanced as a key technology for energy conversion. Recent progress in synthesis, characterization, and computational science has accelerated the discovery of new materials and deepened understanding of their properties. Notable examples include high-efficiency organic–inorganic hybrid perovskites, oxyhalides exhibiting unique visible-light response, and coordination polymers/MOFs with coordination-dependent photophysics and highly selective $CO_2$-to-formate reduction. For practical device applications such as solar cells, improving durability, eliminating toxic or scarce elements, and establishing high-quality synthetic methods are major challenges.

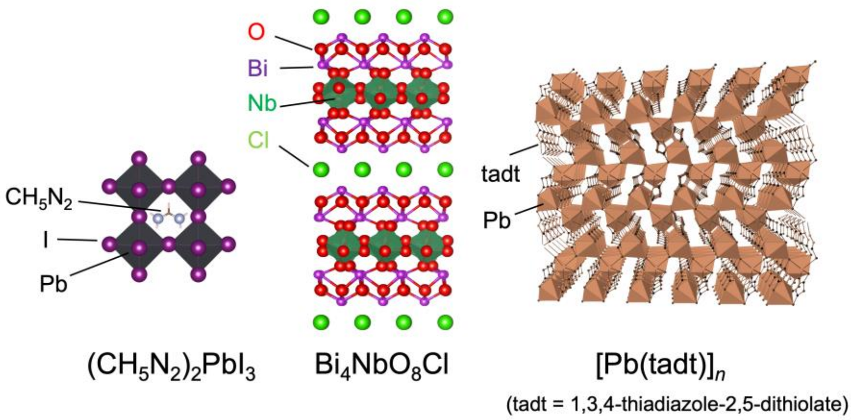


**Figure 1.** Crystal structures of various semiconductors drawn by VESTA.

### Current Status and Frontiers

Research has progressed globally since the 1960s, driven by applications in photocatalytic water splitting. Rising demand for artificial photosynthesis has prompted active exploration of new semiconductor families. Since around 2010, advances in synthesis, computation, and analytical techniques have accelerated new material discovery and clarified fundamental structure–property relationships. Representative developments are outlined below.

**1. Organic–inorganic hybrid perovskites**

Since the seminal work by Miyasaka et al. (2009), hybrid perovskites have rapidly evolved, achieving high-quality solution-processed films, long carrier diffusion lengths, and solar conversion efficiencies exceeding 20%. Progress also includes interface passivation, tandem architectures, applications in LEDs and detectors, and deeper spectroscopic understanding.

**2. Oxyhalides**

Oxyhalides, containing both oxide and halide anion in a single phase, gained attention following $Bi_4NbO_8Cl$ (Abe et al., 2016). Oxyhalides with $Bi^{3+}$ and $Pb^{2+}$ exhibit visible-light response via mechanisms beyond conventional anion p-orbital band engineering. $Pb_2Ti_2O_{5.4}F_{1.2}$, for example, absorbs up to ~500 nm despite containing highly electronegative $F^-$, and has band structures suitable for water splitting.

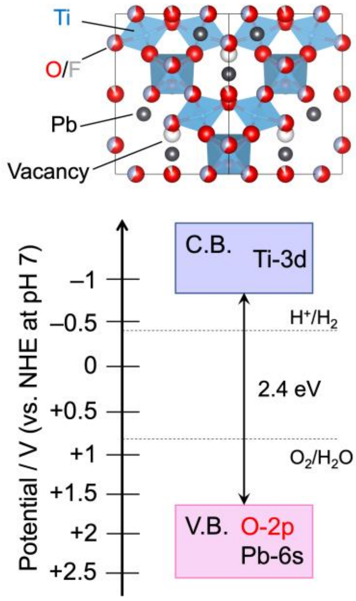


**Figure 2.** Crystal structure and schematic band structure of $Pb_2Ti_2O_{5.4}F_{1.2}$.

**3. Coordination Polymers / MOFs**

Coordination Polymers and metal–organic frameworks (MOFs) with metal–sulfur bonds show semiconducting behavior and coordination-dependent optical properties. Some systems (e.g., $[Pb(tadt)]_n$) display high quantum yields (tens of percent) for selective $CO_2$-to-formate reduction under visible light.

## References


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## Future Perspectives and Directions

Key goals for the next decade include enhanced durability for device applications, development of materials free of toxic or scarce elements, and synthetic methods that ensure high structural and electronic quality.


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