PRESS RELEASE

Sources:
Tokyo Institute of Technology
Chuo University

For immediate release: May 24, 2018, Updated on May 31.

Subject line: Solar energy: Mixed anion compounds with 'fluorine' work as new photocatalytic material
- Novel photocatalyst composed of abundant elements overturns conventional views-

(Tokyo, May 24) Scientists in Japan have shown that an oxyfluoride is capable of visible light-driven photocatalysis[1]. The finding opens new doors for designing materials for artificial photosynthesis and solar energy research.

Over the last decade, research has intensified to develop efficient, manmade photocatalysts that work under visible light — an important target for renewable energy systems.

Now, such efforts have taken a surprising turn, with the discovery of a new photocatalytic material called a pyrochlore[2] oxyfluoride ($Pb_2Ti_2O_{5.4}F_{1.2}$).

Kazuhiko Maeda of Tokyo Institute of Technology (Tokyo Tech), Kengo Oka of Chuo University and collaborators in Japan have succeeded in demonstrating that $Pb_2Ti_2O_{5.4}F_{1.2}$ works as a stable photocatalyst for visible light-driven water splitting and carbon dioxide reduction, with the aid of proper surface modifications.

The new material has an unusually small band gap[3] of around 2.4 electron volts (eV), meaning that it can absorb visible light with a wavelength of around 500 nanometers (nm). In general, band gaps bigger than 3 eV are associated with inefficient utilization of sunlight, whereas those smaller than 3 eV are desirable for efficient solar energy conversion.

What's more, the oxyfluoride belongs to a group of compounds that had until now been largely overlooked due to the highest electronegativity[4] of fluorine, a property that essentially ruled them out as candidates for visible light-driven photocatalysts.

The new oxyfluoride is "an exceptional case", the researchers say in their study published in the *Journal of the American Chemical Society*.

Based on structural considerations and theoretical calculations, they conclude that "the origin of the visible light response in $Pb_2Ti_2O_{5.4}F_{1.2}$ lies in the unique features specific to the pyrochlore-type structure."

Namely, it is the strong interaction between certain orbitals[5] (Pb-6s and O-2p) enabled by short Pb–O bonding in the pyrochlore structure that is thought to give rise to the material's ability to absorb visible light. (See Figure 1.)

One limitation is that the yield of the new photocatalyst currently remains low, at a figure of around 0.01% at 365 nm for hydrogen evolution. The research team is therefore investigating how to boost the yield by modifying $Pb_2Ti_2O_{5.4}F_{1.2}$ through refinement of methods for synthesis and surface modification.

The present study arose as a result of collaborations between institutes including Tokyo Tech, Japan Advanced Institute of Science and Technology (JAIST), the National Institute for Materials Science (NIMS), RIKEN, Kyoto University and Chuo University.

The findings are expected to lead to new directions in materials research and future development of heterogeneous photocatalysts under visible light.

Figure 1. Experiments reveal the strong visible-light absorption of $Pb_2Ti_2O_{5.4}F_{1.2}$
The inset (on the right) shows a photograph of $Pb_2Ti_2O_{5.4}F_{1.2}$, which is capable of absorbing visible light. This ability is thought to be due to strong interaction between Pb and O, which is enabled by the short Pb-O bond in the pyrochlore lattice.

Technical terms

[1] Visible light-driven photocatalysis: The process of converting solar to fuel energy using visible-light-absorbing semiconductor materials.

[2] Pyrochlore : One of crystal structures represented by a chemical formula of $A_2B_2X_6X'$, where A and B show cations, X and X' show anions. The A and B elements are generally rare-earth or transition metal elements. The presence of two short bonds between A site ion (Pb) and X' site (O) is the characteristic of this structure.

[3] Band gap: Refers to the difference in energy of an electron in the valence band and the conduction band, which indicates the conductivity of a material.

[4]Electronegativity: A property whereby electrons are held tightly to the nucleus. Fluorine has the highest electronegativity among all elements.

[5] Orbitals: The regions where electrons can be calculated to be present within atoms.

References

Ryo Kuriki[1,2], Tom Ichibha[3], Kenta Hongo[4,5,6,7], Daling Lu[8], Ryo Maezono[3,7], Hiroshi Kageyama[9], Osamu Ishitani[1], Kengo Oka[10], and Kazuhiko Maeda*[1], A Stable, Narrow-Gap Oxyfluoride Photocatalyst for Visible-Light Hydrogen Evolution and Carbon Dioxide Reduction, *Journal of the American Chemical Society*. DOI: 10.1021/jacs.8b02822
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