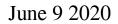
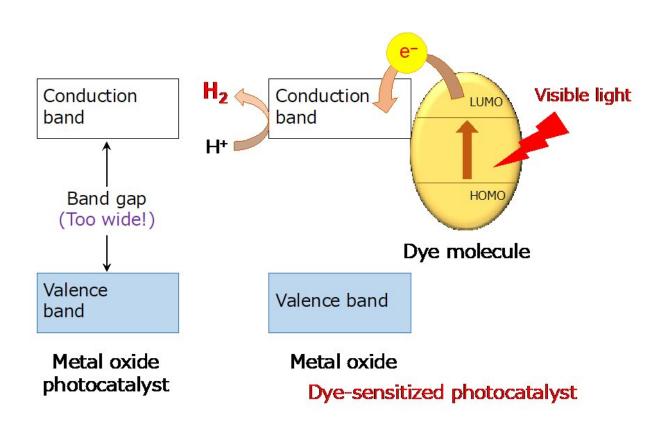


New nanomaterial developed to split water molecules, obtain dihydrogen under sunlight





A new photocatalyst consisting of nanoscale metal oxide sheets and a ruthenium dye molecule can generate H_2 from water by utilizing visible light. Credit: Tokyo Tech

Scientists at Tokyo Institute of Technology (Tokyo Tech) have developed a hybrid material constructed from a metal oxide nanosheet



and a light-absorbing molecule for splitting water molecules to obtain dihydrogen (H_2) under sunlight. Since H_2 can be used as carbon-free fuel, this study provides relevant insight toward clean energy generation.

In line with the depletion of fossil fuels and the environmental problems due to their combustion, developing technology for clean energy generation is a topic of global interest. Among the various methods proposed to generate clean energy, photocatalytic <u>water</u> splitting is showing much promise. This method utilizes solar energy to split <u>water</u> molecules and obtain dihydrogen (H₂). The H₂ can then be used as a carbon-free fuel or as raw material in the production of many important chemicals.

Now, a research team led by Kazuhiko Maeda at Tokyo Tech has developed a new photocatalyst consisting of nanoscale metal oxide sheets and a ruthenium dye molecule, which works according to a mechanism similar to dye-sensitized solar cells. While metal oxides that are photocatalytically active for overall water splitting into H_2 and O_2 have wide band gaps, dye-sensitized oxides can utilize visible light, the main component of sunlight (Figure 1). The new photocatalyst is capable of generating H_2 from water with a turnover frequency of 1960 per hour and an external quantum yield of 2.4%.

These results are the highest recorded for dye-sensitized photocatalysts under visible light, bringing Maeda's team a step closer to the goal of artificial photosynthesis—replicating the natural process of using water and sunlight to sustainably produce energy.

The new material, reported in *Journal of the American Chemical Society*, is constructed from high-surface-area calcium niobate nanosheets $(HCa_2Nb_3O_{10})$ intercalated with platinum (Pt) nanoclusters as H_2 -evolving sites. However, the platinum-modified nanosheets do not work alone, as they do not absorb sunlight efficiently. So a visible light-



absorbing ruthenium dye molecule is combined with the <u>nanosheet</u>, enabling solar-driven H_2 evolution (Figure 2).

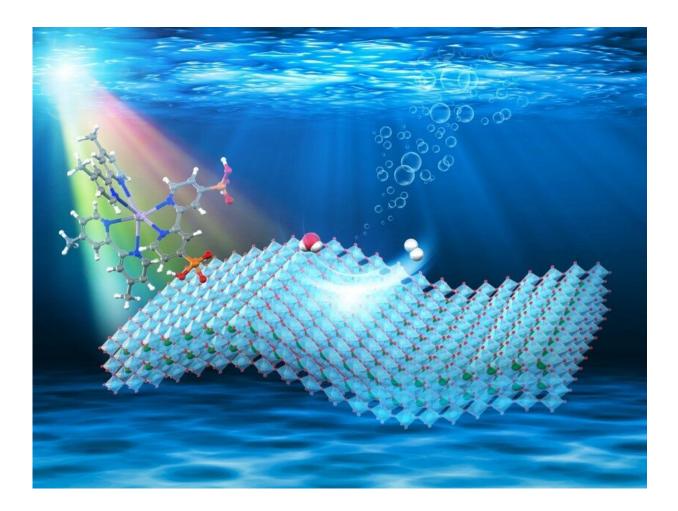


Illustration of visible-light-driven H_2 evolution on ruthenium-dye/HCa₂Nb₃O₁₀ nanosheet. Credit: American Chemical Society, Tokyo Tech, adopted with permission

What makes the material efficient is the use of nanosheets, which can be obtained by chemical exfoliation of lamellar $HCa_2Nb_3O_{10}$. The high-surface-area and structural flexibility of the nanosheets maximize dye-loadings and density of H₂ evolution sites, which in turn improve H₂



evolution efficiency. Also, to optimize performance, Maeda's team modified the nanosheets with amorphous alumina, which plays an important role in improving electron transfer efficiency. "Unprecedentedly, the alumina modification for nanosheets promotes dye-regeneration during the reaction without hindering electron injection from the excited-state dye to the nanosheet—the primary step of dyesensitized H₂ evolution," Maeda says.

"Until just recently, it was considered very difficult to achieve H_2 evolution via overall water splitting under <u>visible light</u> using a dyesensitized photocatalyst with high efficiency," explains Maeda. "Our new result clearly demonstrates that this is indeed possible, using a carefully designed molecule-nanomaterial hybrid."

More research is required, as it will be necessary to further optimize the design of the hybrid photocatalyst to improve the efficiency and long-term durability. Photocatalytic water splitting may be a crucial means of meeting society's energy demands without further harming the environment, and studies like this one are essential stepping stones to reaching our goal of a greener future.

More information: Takayoshi Oshima et al, An Artificial Z-Scheme Constructed from Dye-Sensitized Metal Oxide Nanosheets for Visible Light-Driven Overall Water Splitting, *Journal of the American Chemical Society* (2020). DOI: 10.1021/jacs.0c02053

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