Highly efficient hydrogen gas production using sunlight, water and hematite

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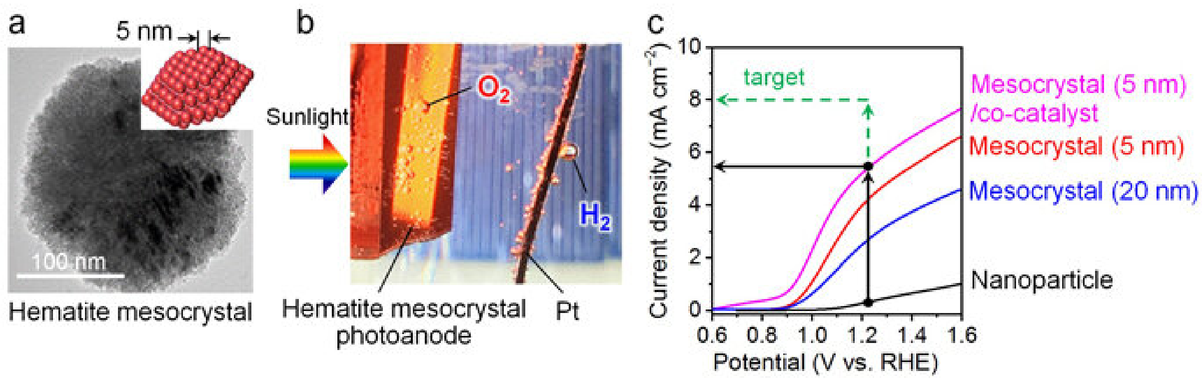


Mesocrystal photoanode formation and photochemical water splitting characteristics. a. Electron microscope image of a hematite mesocrystal (assembled from tiny nano-particles of approx. 5nm). b. Gas production from the anode. c. Graph to show the current density and applied voltage. The anode is the photocatalyst anode, and a platinum electrode was used for the cathode. The potential is based on the RHE (Reversible Hydrogen Electrode). The oxidation potential is 1.23V. The solar water splitting capacity was greatly enhanced by making the nano-particles in the mesocrystal structures smaller. Credit: Kobe University

A research group led by Associate Professor Tachikawa Takashi of Kobe University's Molecular Photoscience Research Center has succeeded in developing a strategy that greatly increases the amount of hydrogen produced from sunlight and water using hematite photocatalysts.

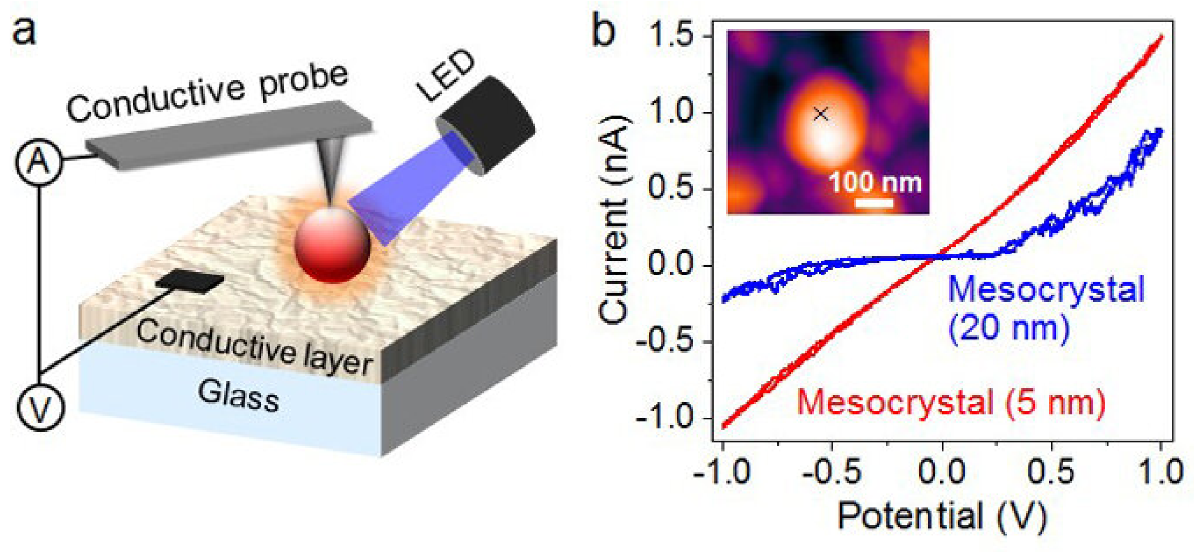
Hydrogen has received attention as a possible next generation energy solution, and it can be produced from sunlight and water using photocatalysts. In order to make this practicable, it is necessary to develop foundation technologies to optimize the potential of the photocatalysts, in addition to finding new materials for catalysts.

This time, Tachikawa et al. successfully produced a photoanode with an extremely high conductivity. This was achieved solely by annealing hematite mesocrystals, (superstructures consisting of tiny nanoparticles of approx. 5nm) to a transparent electrode substrate. Hematite can absorb a wide range of visible light and is safe, stable, and inexpensive.

With this photoanode, the electrons and holes produced by the light source separated quickly and, at the same time, a large number of holes densely accumulated on the surface of the particles. The accumulation of holes improved the efficiency of the water oxidation reaction; the slow oxidation of the water has previously been a bottleneck in water-splitting.

In addition to boosting the high efficiency of what is thought to be the world's highest performing photoanode, this strategy will also be applied to artificial photosynthesis and solar water-splitting technologies via collaborations between the university and industries.

These results will be published in the German online chemistry journal *Angewandte Chemie International Edition* on April 30. This work was also featured in the inside cover.



The photoconductivity of the hematite mesocrystals. a. Illustration of the photoconductive AFM (*10) measurements. b. Graph showing the corresponding current/current potential curves. The inset image shows the measured mesocrystal (produced from sintering mesocrystals from tiny 5nm nanoparticles). Credit: Kobe University

Main points:

- Numerous oxygen vacancies were formed inside the hematite mesocrystals by accumulating and sintering tiny highly-orientated nanoparticles of less than 10 nanometers.
- The presence of oxygen vacancies improved the conductivity of the photocatalyst electrode, at the same time giving it a significant surface potential gradient, thereby promoting the separation of electrons and holes.
- At the same time a large amount of holes moved to the surface of the particles, allowing a high rate of oxygen evolution from water. This enabled the researchers to achieve the world's highest

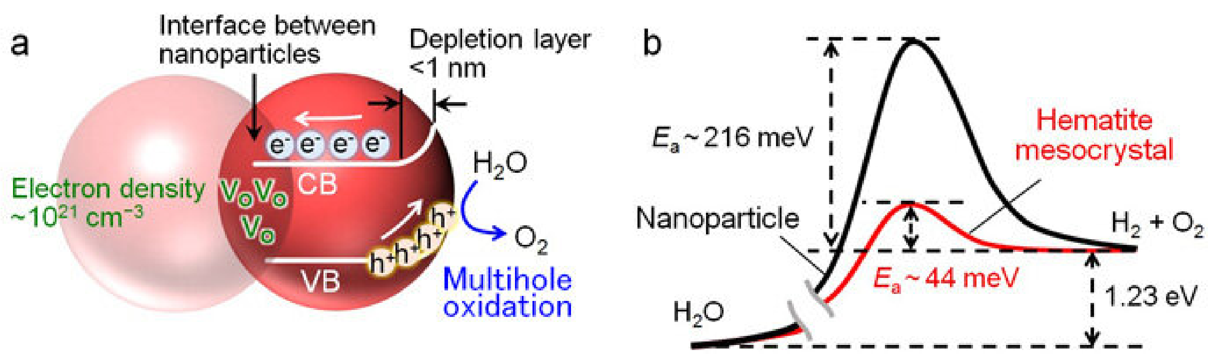
solar water-splitting performance for hematite anodes.
- This strategy can be applied to a wide range of photocatalysts, beginning with solar water-splitting.

With the world facing increasing environmental and energy issues, hydrogen has gained attention as one of the possible next generation energy sources. Ideally, photocatalysts could be used to convert water and sunlight into hydrogen. However, a solar energy conversion rate of over 10% is necessary to enable such a system to be adopted industrially. Utilizing Japan's strengths in new materials discovery, it is vital to establish a common foundation technology that can unlock the potential of photocatalysts in order to achieve this aim.

Previously, Tachikawa et al. developed 'mesocrystal technology', which involves precisely aligning nanoparticles in photocatalysts to control the flow of electrons and their holes. Recently, they applied this technology to hematite (a-Fe_2O_3), and succeeded in dramatically increasing the conversion rate.

This time, they were able to raise the conversion rate up to 42% of its theoretical limit (16%) by synthesizing tiny nanoparticle subunits in the hematite.

Mesocrystal technology:



The solar water splitting mechanism of hematite mesocrystals. a. The formation of oxygen vacancies (Vo) inside the mesocrystals and band structure. Depletion layers of less than 1nm promote the electron division and water oxidation. CB: Conduction Band, VB: Valence Band, e-: electron, h+: hole. b. In accordance to the potential gradient, a large amount of holes accumulated on the particle surface and oxidized the water, leading to a large decrease in the activation energy (Ea) and improving the conversion rate.

The main problem that causes a conversion rate decline in photocatalytic reactions is that the electrons and holes produced by light recombine before they can react with the molecules (in this case, water) on the surface. Tachikawa et al. created hematite mesocrystal superstructures with highly oriented nanoparticles via solvothermal synthesis. They were able to develop conductive mesocrystal photoanodes for water splitting by accumulating and sintering mesocrystals onto the transparent electrode substrate (Figure 1).

Photocatalyst formation and performance:

Mesocrystal photoanodes were produced by coating the transparent electrode substrate with hematite mesocrystals containing titanium and then annealing them at 700 ºC. A co-catalyst was deposited on the surface of the mesocrystals. When the photocatalysts were placed in an alkaline solution and illuminated with artificial sunlight, the water-splitting reaction took place at a photocurrent density of 5.5mAcm-2 under an applied voltage of 1.23V (Figure 1). This is the highest performance achieved in the world for hematite, which is one of the most ideal photocatalyst materials due to both its low cost and light absorption properties. In addition, the hematite mesocrystal photoanodes functioned stably during repeated experiments over the course of 100 hours.

The key to achieving a high conversion rate is the size of the nanoparticles that make up the mesocrystal structure. It is possible to greatly increase the amount of oxygen vacancies that form during the sintering process by making the nanoparticles as small as 5 nm and increasing the connecting interfaces between the nanoparticles. This boosted the electron density, and significantly increased the conductivity of the mesocrystals (Figure 2).

The high electron density is connected to the formation of a large band bending near the mesocrystal surface. This promotes the initial charge separation as well as making it easier for holes to accumulate on the surface. This result was optimized due to the tiny nanoparticle structure of the mesocrystals, and boosted the water oxidation reaction that had been a bottleneck for efficient water-splitting (Figure 3).

This study revealed that mesocrystal technology is able to significantly minimize the recombination issue, which is the main cause of low efficiency in photocatalysts, and exponentially accelerate the water splitting reaction.

It is hoped that this strategy can be applied to other metal oxides as well. Next, the researchers will collaborate with industries to optimize the hematite mesocrystal photoanodes and implement an industrial system for producing hydrogen from solar light. At the same time, the strategy developed by this study will be applied to various reactions, including artificial photosynthesis.

More information: Zhujun Zhang et al, Ultra-Narrow Depletion Layers in a Hematite Mesocrystal-Based Photoanode for Boosting Multihole Water Oxidation, *Angewandte Chemie International Edition* (2020). DOI: 10.1002/anie.202001919

Provided by Kobe University