

## Lighting Up Enzymes for Solar Hydrogen Production

Hybrid molecular assemblies composed of hydrogenase enzymes and quantum dots helps to pave the way for the development of next-generation photocatalytic materials for water-to-hydrogen conversion technologies.

Scientists at the National Renewable Energy Laboratory (NREL) have combined quantum dots, which are spherical nanoparticles that possess unique size-tunable photo-physical properties, with the high substrate selectivity and fast turnover of hydrogenase enzymes to achieve light-driven hydrogen ( $H_2$ ) production. They found that quantum dots of cadmium telluride coated in carboxylic acids easily formed highly stable complexes with the hydrogenase and that these hybrid assemblies functioned to catalyze  $H_2$  production using the energy of sunlight.

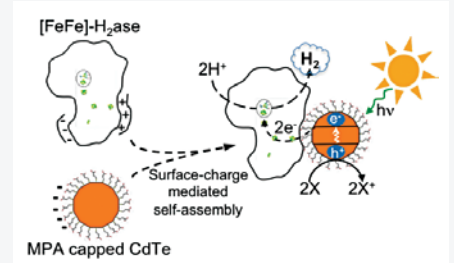
During biological photosynthesis, ferredoxin functions to mediate the transfer of photoexcited electrons to hydrogenase, which results in light-driven  $H_2$  production. This interaction of hydrogenase with ferredoxin during electron transfer relies on surface charge interactions such that the positive (hydrogenase) and the negative (ferredoxin) regions can interact.

In the biohybrid, the negatively charged carboxylic acid-coated quantum dot was able to interact with the positively charged hydrogenase in a way that allowed it to replace ferredoxin as the electron source for the hydrogenase. Optical measurements showed that the photocatalytic efficiency varied with the quantum dot/hydrogenase ratio, which was maximal at low enzyme coverages favoring one-to-one ratios.

The efficiency of photocatalytic  $H_2$  production was also a direct function of the intrinsic quantum dot photoluminescent quantum efficiency. Higher quantum efficiencies led to higher  $H_2$  production rates.

In summary, carboxylic acid-coated quantum dots and hydrogenase spontaneously assemble into complexes that, on illumination, transfer photo-generated electrons from quantum dot core states to the hydrogenase, resulting in  $H_2$  production from water. Low hydrogenase coverages promoted optimal orientations for solar  $H_2$  production.

**Reference:** Brown, Katherine A.; Dayal, Smita; Ai, Xin; Rumbles, Garry; and King, Paul W. "Controlled Assembly of Hydrogenase-CdTe Nanocrystal Hybrids for Solar Hydrogen Production." *Journal of the American Chemical Society*, June 28, 2010.



### Key Research Results

#### Achievement

NREL researchers developed new, hybrid materials that function as  $H_2$  producing photocatalysts.

#### Key Result

Carboxylic acid-coated quantum dots and hydrogenase spontaneously assemble into complexes that, on illumination, transfer photo-generated electrons from quantum dot core states to the hydrogenase, resulting in  $H_2$  production.

#### Potential Impact

This collaboration of NREL's Biosciences and Materials Sciences Centers has led to a breakthrough that can help guide the development of artificial solar-to-hydrogen processes to become more efficient, viable technologies.