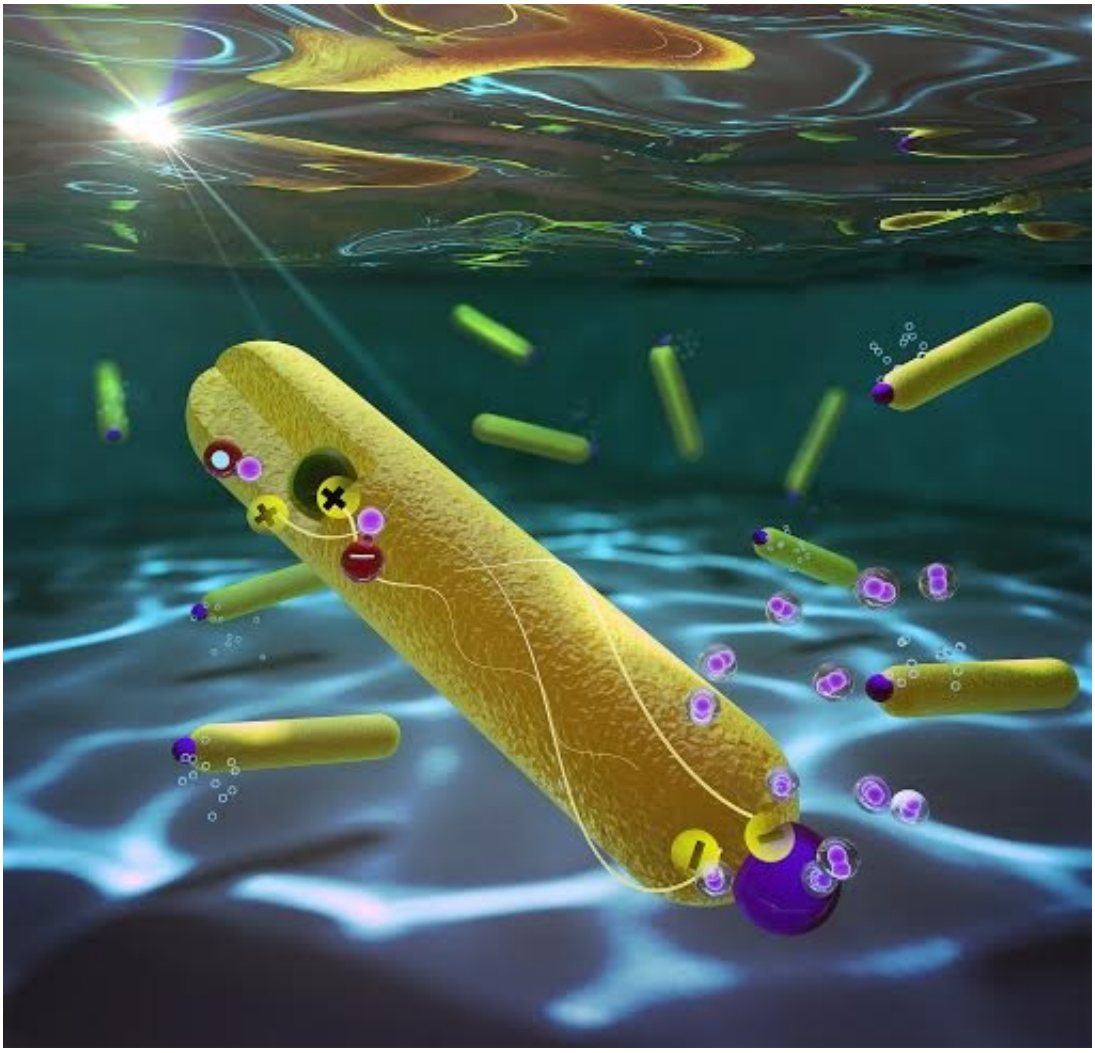
Scientists achieve perfect efficiency for water-splitting half-reaction

February 26 2016, by Lisa Zyga



Under visible light illumination, the nanoscale photocatalysts perform the water-splitting reduction half-reaction with 100% efficiency. Credit: Lilac Amirav, Technion-Israel Institue of Technology

(Phys.org)—Splitting water is a two-step process, and in a new study, researchers have performed one of these steps (reduction) with 100% efficiency. The results shatter the previous record of 60% for hydrogen production with visible light, and emphasize that future research should focus on the other step (oxidation) in order to realize practical overall water splitting. The main application of splitting water into its components of oxygen and hydrogen is that the hydrogen can then be used to deliver energy to fuel cells for powering vehicles and electronic devices.

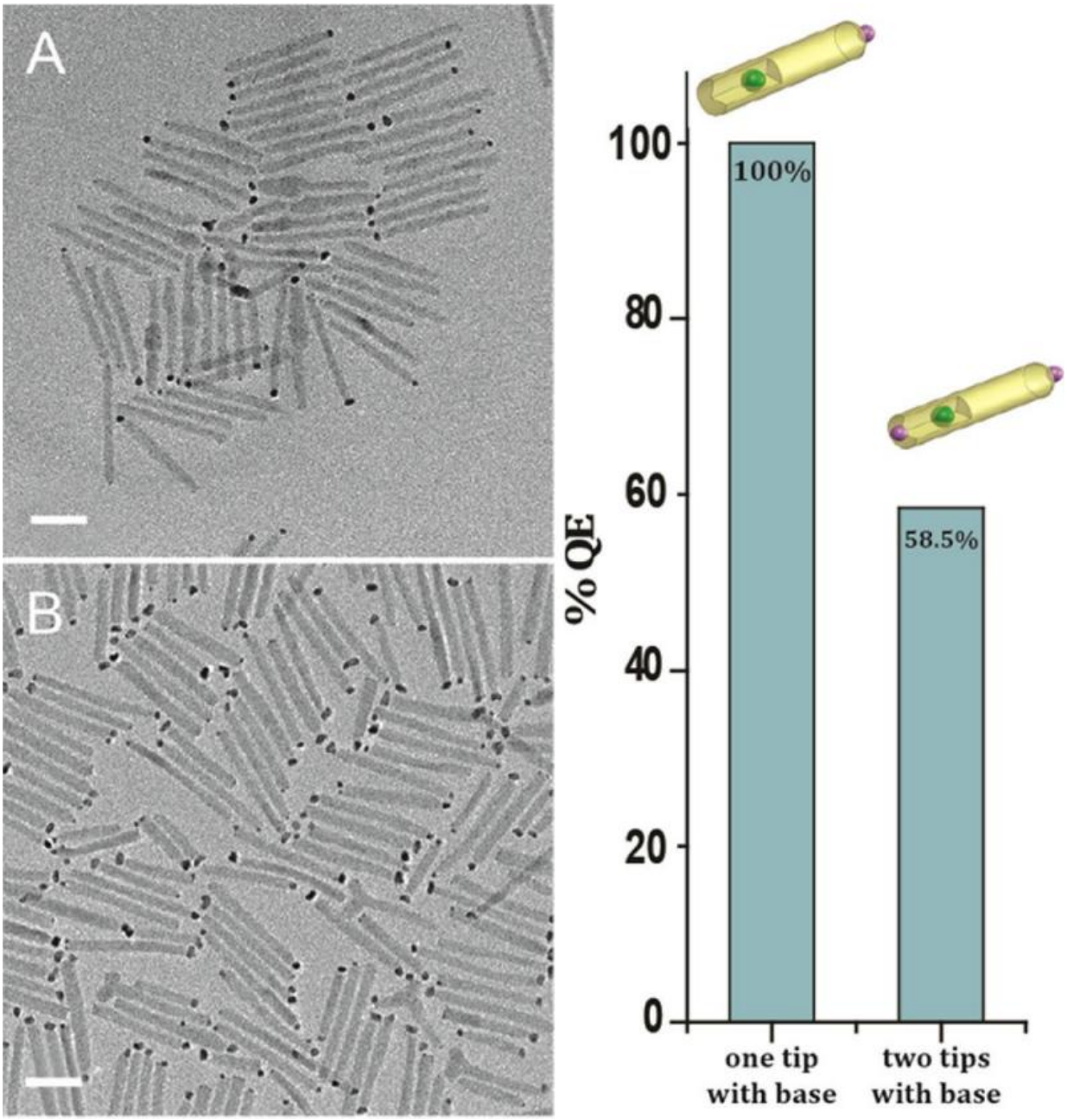
The researchers, Philip Kalisman, Yifat Nakibli, and Lilac Amirav at the Technion-Israel Institute of Technology in Haifa, Israel, have published a paper on the perfect efficiency for the water reduction half-reaction in a recent issue of *Nano Letters*.

"I strongly believe that the search for clean and renewable energy sources is crucial," Amirav told *Phys.org*. "With the looming energy crisis on one hand, and environmental aspects, mainly global warming, on the other, I think this is our duty to try and amend the problem for the next generation.

"Our work shows that it is possible to obtain a perfect 100% photon-to-hydrogen production efficiency, under visible light illumination, for the photocatalytic water splitting reduction half-reaction. These results shatter the previous benchmarks for all systems, and leave little to no room for improvement for this particular half-reaction. With a stable system and a turnover frequency of 360,000 moles of hydrogen per hour per mole of catalyst, the potential here is real."

When an H_2O molecule splits apart, the three atoms don't simply separate from each other. The full reaction requires two H_2O molecules to begin with, and then proceeds by two separate half-reactions. In the oxidation half-reaction, four individual hydrogen atoms are produced

along with an O_2 molecule (which is discarded). In the reduction half-reaction, the four hydrogen atoms are paired up into two H_2 molecules by adding electrons, which produces the useful form of hydrogen: H_2 gas.



(Left) Transmission electron microscope images of the nanorod photocatalysts

with (a) one and (b) two platinum tips. (Right) A comparison of the efficiencies shows the advantage of using a single platinum tip. Credit: Kalisman, et al. ©2016 American Chemical Society

In the new study, the researchers showed that the reduction half-reaction can be achieved with perfect efficiency on specially designed 50-nm-long nanorods placed in a water-based solution under visible light illumination. The light supplies the energy required to drive the reaction forward, with the nanorods acting as photocatalysts by absorbing the photons and in turn releasing electrons needed for the reaction.

The 100% efficiency refers to the photon-to-hydrogen conversion efficiency, and it means that virtually all of the photons that reach the photocatalyst generate an electron, and every two electrons produce one H_2 molecule. At 100% yield, the half-reaction produces about 100 H_2 molecules per second (or one every 10 milliseconds) on each nanorod, and a typical sample contains about 600 trillion nanorods.

One of the keys to achieving the perfect efficiency was identifying the bottleneck of the process, which was the need to quickly separate the electrons and holes (the vacant places in the semiconductor left after the electrons leave), and remove the holes from the photocatalyst. To improve the charge separation, the researchers redesigned the nanorods to have just one platinum catalyst instead of two. The researchers found that the efficiency increased from 58.5% with two platinum catalysts to 100% with only one.

Going forward, the researchers plan to further improve the system. The current demonstration requires a very high pH, but such strong basic conditions are not always ideal in practice. Another concern is that the cadmium sulfide (CdS) used in the nanorod becomes corroded under

prolonged light exposure in pure water. The researchers are already addressing these challenges with the goal to realize practical solar-to-fuel technology in the future.

"We hope to implement our design rules, experience and accumulated insights for the construction of a system capable of overall water splitting and genuine solar-to-fuel energy conversion," Amirav said. "The photocatalytic hydrogen generation presented here is not yet genuine solar-to-fuel energy conversion, as hole scavengers are still required. CdS is unfortunately not suitable for overall water splitting since prolonged irradiation of its suspensions leads to photocorrosion. We have recently demonstrated some breakthrough on this direction as well. The addition of a second co-catalyst, such as IrO_2 or Ru, which can scavenge the holes from the semiconductor and mediate their transfer to water, affords CdS-based structures the desired photochemical stability. I believe this is an important milestone."

More information: Philip Kalisman, et al. "Perfect Photon-to-Hydrogen Conversion Efficiency." *Nano Letters*. DOI: 10.1021/acs.nanolett.5b04813

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