Tripling the efficiency of solar-based hydrogen fuel generation with metallic nanostructures that slow down light

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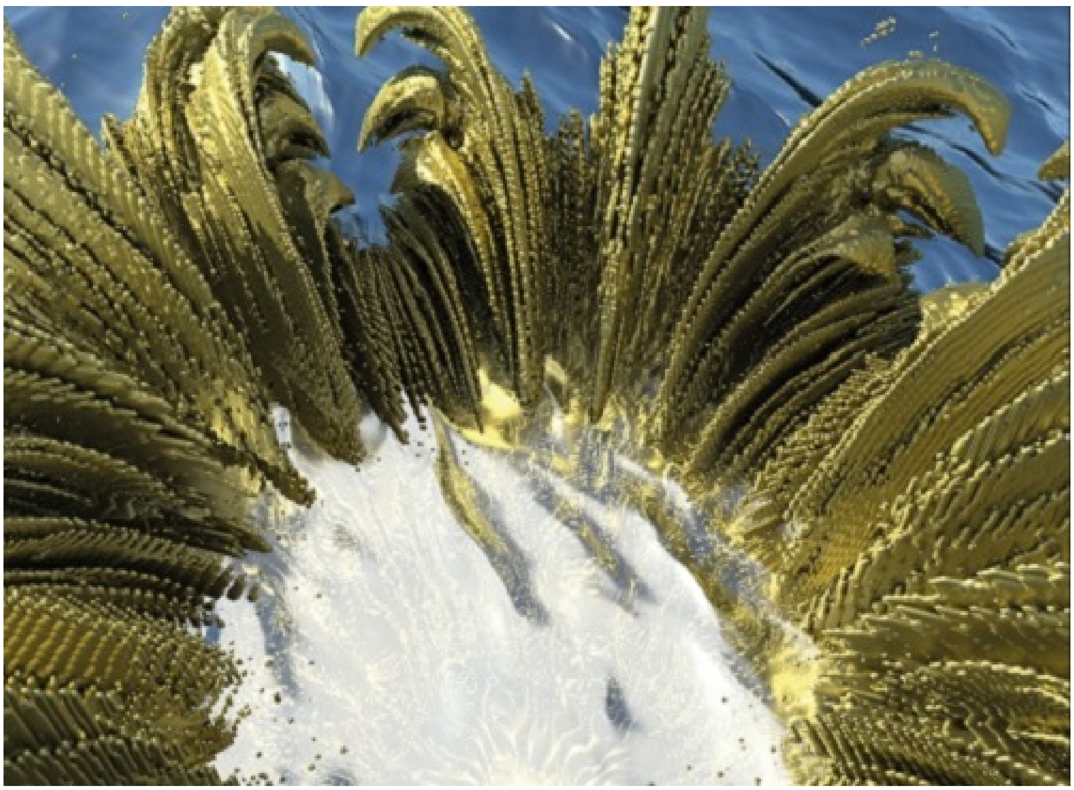

A nanostructured metamaterial with a sunflower-like arrangement can be immersed in water to generate hydrogen gas with superb efficiency. Credit: WILEY-VCH Verlag GmbH & Co.

Hydrogen gas, an important synthetic feedstock, is poised to play a key role in renewable energy technology; however, its credentials are undermined because most is currently sourced from fossil fuels, such as natural gas. A KAUST team has now found a more sustainable route to hydrogen fuel production using chaotic, light-trapping materials that mimic natural photosynthetic water splitting.

The complex enzymes inside plants are impractical to manufacture, so researchers have developed photocatalysts that employ high-energy, hot electrons to cleave water molecules into hydrogen and oxygen gas. Recently, nanostructured metals that convert solar electrons into intense, wave-like plasmon resonances have attracted interest for hydrogen production. The high-speed metal plasmons help transfer carriers to catalytic sites before they relax and reduce catalytic efficiency.

Getting metal nanoparticles to respond to the entire broadband spectrum of visible light is challenging. "Plasmonic systems have specific geometries that trap light only at characteristic frequencies," explains Andrea Fratalocchi, who led the research. "Some approaches try to combine multiple nanostructures to soak up more colors, but these absorptions take place at different spatial locations so the sun's energy is not harvested very efficiently."

Fratalocchi and his team devised a new strategy using metal nanostructures known as epsilon-near-zero (ENZ) metamaterials that grow with random, fractal needles similar to a tiny pine tree. Inside the cavities formed by the protruding metal branches, the propagation of light slows to a near standstill. This enables the ENZ substance to squeeze all visible light colors to the same nanometer-scale locations.

However, optimizing the ENZ material for hydrogen generation proved a protracted process of months. Not every needle-like structure works the same way, which meant the team had to fine tune all fabrication parameters to find the correct disorder for efficient reactions. Then, choosing semiconducting titanium dioxide as a substrate to collect hot electrons required crystals with extremely high purity. Finally, the concentration and position of platinum nanoparticles used to catalytically split water molecules needed to be precisely controlled, depositions that are difficult with ENZ's complex geometry.

The result was worth the perseverance: experiments revealed the ENZ photocatalyst used broadband light to generate hot carriers within a narrow 10-nm interfacial region for an overall 300% gain in efficiency.

"Due to the possibility of controlling their absorption, the ENZ nanostructures are ideal candidates for solar-energy harvesting," says Fratalocchi. "We recently engineered an industrial prototype with impressive efficiency, which makes us very optimistic about the future possibilities of this technology."

More information: Yi Tian et al. Enhanced Solar-to-Hydrogen Generation with Broadband Epsilon-Near-Zero Nanostructured Photocatalysts, *Advanced Materials* (2017). DOI: 10.1002/adma.201701165

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