

Title: Nanostars shine in light-driven water reduction

Summary:

The “alchemy of water”, i.e. turning water into fuel (i.e. hydrogen) with sunlight is an exciting prospect for sustainable energy. In a recent *Chem* issue Atta et al. developed plasmonic-TiO₂ nanostructures that bring photocatalytic water splitting one step closer to reality.

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Turning abundant, inert chemicals into valuable substances has inspired researchers for centuries. Historically, turning iron to gold motivated much experimentation, modern-day “alchemists” also dream of turning cheap, abundant molecules to useful ones. One of the most exciting chemical reactions in this class is the production of hydrogen from water using sunlight, a staggeringly difficult reaction where material design is poised to be part of the solution.

A key issue in photocatalytic water splitting is that visible photons interact weakly with water. Shining light on water indeed doesn't spontaneously split it (as one can observe in everyday life). Careful design of a device to trap and channel light into powering this chemical reaction is thus needed.

Recently, much excitement has been generated by localized surface plasmon resonances' (LSPR's) ability to interact with light; LSPRs can in fact have absorption cross-sections larger than their physical size, which ranges from few tens to hundreds of nanometers.¹⁻³ LSPRs concentrate (sun)light's energy and confine it to sub-wavelength regions at the surface of a nanoparticle. Once harvested, this energy could, in principle, be used to drive chemical reactions.⁴ However, efficiently turning light to chemical energy using LSPRs requires further materials development to enhance the coupling between molecules and plasmonic effects, such as the addition of catalytic surfaces and semiconductor structures.^{4,5}

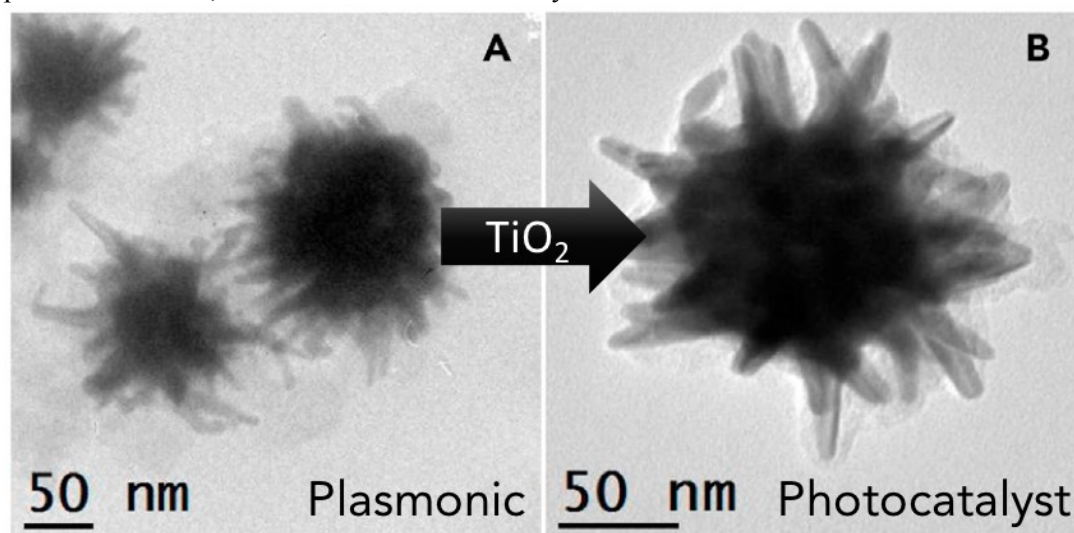


Figure 1. The crystalline TiO₂ coatings developed by Atta et al. make Au nanostars photocatalytically active for water splitting under broadband sun-like illumination.

In a recent *Chem* paper, Atta et al.⁶ contribute an exciting novel structure to the burgeoning field of plasmon-enhanced photocatalysis. The authors describe synthetic protocols that combine two technologies to move one step closer to sun-driven hydrogen production. Their spiky gold nanostars first trap abundant infrared light at their surfaces via the nanoparticle's plasmon resonances. Then, the energy associated with this excitation is transferred to a TiO₂ coating that efficiently drives photocatalytic water splitting.

One of the novel aspects of the author's research is the low-temperature hydrothermal treatment of the TiO₂. This allows the production of a crystalline TiO₂ coating while preserving the temperature-sensitive morphology of the nanostars (Figure 1). Nanostars treated such that the crystallinity of the shell is maximized, yielding a mix of anatase and rutile, showed an enhanced photocatalytic activity under broadband, sun-like illumination, significantly higher than other shell crystallinities. They could further single out that the reaction is driven by the infrared LSPRs rather than direct absorption into the UV-bandgap TiO₂: illumination with either UV or visible light yielded up to an order of magnitude less hydrogen.

The "alchemy of water" still poses challenges, including for instance scale-up and the development of broadband absorption. The shiny nanostars developed by Atta et al.⁶ bring photocatalytic water splitting one step closer to reality.

References

1. Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B* **2003**, *107*, 668-677.
2. Eustis, S.; El-Sayed, M. A. Why Gold Nanoparticles Are More Precious Than Pretty Gold: Noble Metal Surface Plasmon Resonance and Its Enhancement of the Radiative and Nonradiative Properties of Nanocrystals of Different Shapes. *Chemical Society Reviews* **2006**, *35*, 209-217.
3. Ozbay, E. Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions. *Science* **2006**, *311*, 189.
4. Warren, S. C.; Thimsen, E. Plasmonic Solar Water Splitting. *Energy & Environmental Science* **2012**, *5*, 5133-5146.
5. Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nature Materials* **2011**, *10*, 911.
6. Atta, S.; Pennington, A. M.; Celik, F. E.; Fabris, L. TiO₂ on Gold Nanostars Enhances Photocatalytic Water Reduction in the near-Infrared Regime. *Chem* **2018**. DOI: 10.1016/j.chempr.2018.06.004.