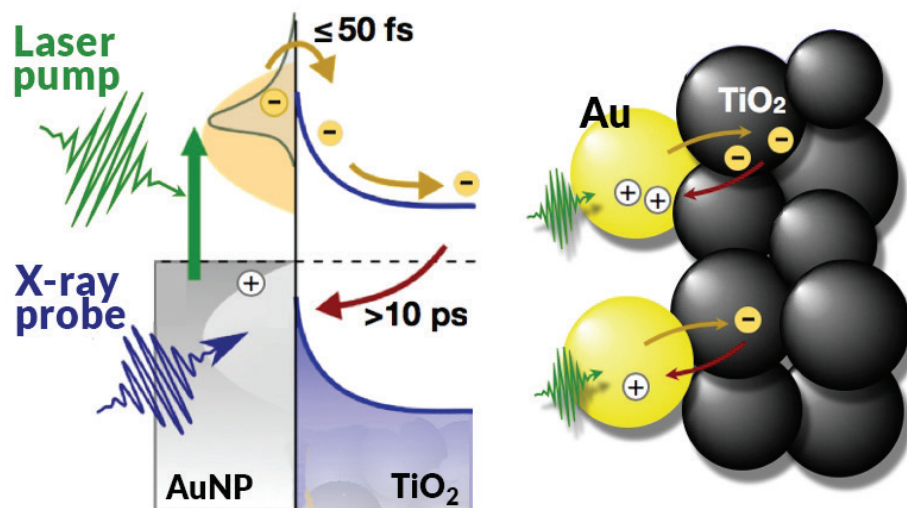
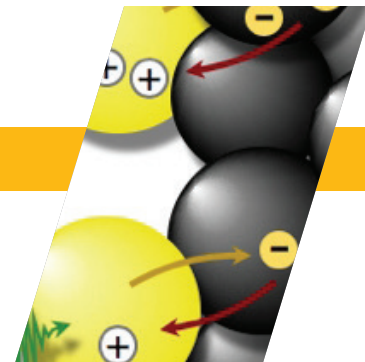


# A Probe of Light-Harvesting Efficiency at the Nanoscale



Laser pulses were used to excite electrons in gold nanoparticles (AuNPs) on a titanium dioxide (TiO<sub>2</sub>) substrate. X-ray pulses were used to count the electrons moving between the nanoparticles and the substrate. (Credit: Oliver Gessner/Berkeley Lab)

## Solar-fuel tech goes for gold

In the search for clean-energy alternatives to fossil fuels, one promising solution relies on photoelectrochemical (PEC) cells: water-splitting, artificial-photosynthesis devices that turn sunlight and water into solar fuels such as hydrogen. In just a decade, researchers have achieved great progress in the development of PEC systems made of light-absorbing gold nanoparticles (NPs) attached to a semiconductor film of titanium dioxide (TiO<sub>2</sub>).

Despite these advancements, researchers still struggle to make a device that can produce solar fuels on a commercial scale. To explain why some water-splitting PEC devices do not work as well as hoped, researchers have now quantified electron transfers between gold and TiO<sub>2</sub> at the nanoscale and in real time. The

results should help researchers develop more-efficient material combinations for high-performance solar-fuel devices.

## A productive pairing comes to light

When illuminated by sunlight, electrons in gold NPs move in sync with the electric field of the light (“plasmonic resonance”). Some of the electrons pass through the gold/TiO<sub>2</sub> interface, leaving holes behind. These electron-hole pairs are critical ingredients for enabling the chemical reaction that produces solar fuels. The longer the lifetime of the electron-hole pairs, the more time there is for the chemical reaction to take place.

Thus, to understand how efficiently a PEC device is working, it’s necessary to know the number of electrons moving

## Scientific Achievement

Using time-resolved experiments at the Advanced Light Source (ALS), researchers found a way to count electrons moving back and forth across a model interface for photoelectrochemical cells.

## Significance and Impact

The findings provide real-time, nanoscale insight into the efficiency of nanomaterial catalysts that help turn sunlight and water into fuel through artificial photosynthesis.

between the gold and TiO<sub>2</sub> as well as how long the electron-hole pairs last. By tracing the movement of electrons in these complex systems with chemical specificity and picosecond time resolution, an accurate calculation of the conversion efficiency of plasmonic light-harvesting devices can be obtained.

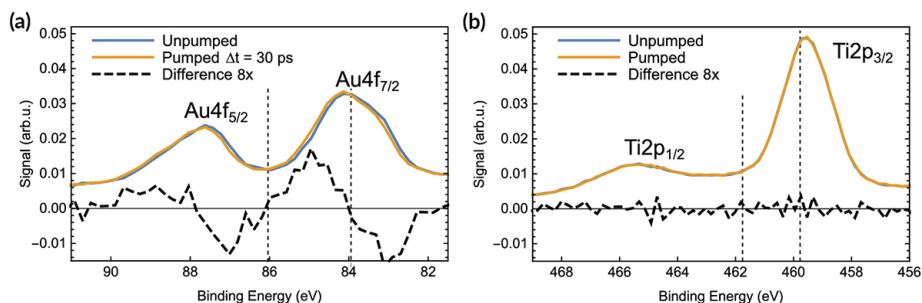
## An electronic “count”-down

At ALS Beamline 11.0.2, researchers performed time-resolved, pump-probe x-ray photoelectron spectroscopy (XPS) experiments in which pulses of laser light were used to excite electrons in gold NPs on a TiO<sub>2</sub> film. Delayed x-ray pulses then probed both the electron donor (Au) and acceptor (Ti) materials. Comparison of the excited- and ground-state spectra revealed a shift in the excited Au spectrum

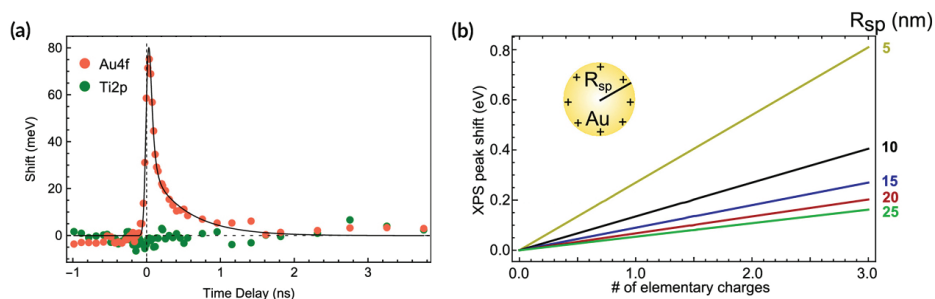
to higher binding energies, but no observable effect in the Ti.

Analysis of the time dependence of the shift in Au spectra indicated a time scale of about 1 ns for the electron-hole pair lifetime. The number of electrons transferred was obtained by modeling the shift in binding energy as being due to a constant potential created by the accumulation of excess or missing charge at the NP surface. The model predicts that the number of electrons transferred is linearly dependent on the shift in binding energy. In this case, that meant approximately two electrons were transferred per NP—far fewer than expected. The corresponding photon-to-charge conversion efficiency was 0.1%.

Although XPS is commonly used around the world, this work is a unique expansion of the technique to time-resolved studies and is the first time it has been applied to charge-transfer dynamics in nanoplasmonic systems. The research team next plans to push their measurements to even faster time scales with a free-electron laser and to capture even finer nanoscale snapshots of electrons at work in a PEC device when water is added to the mix.



Comparison of the (a) Au and (b) Ti spectra before excitation (blue) and at a pump-probe delay of  $\Delta t = 30$  ps (orange). The dashed black lines indicate the differences between the excited- and ground-state spectra, multiplied by a factor of 8 for better visibility.



(a) Site-specific, time-dependent photoresponse of the AuNP/TiO<sub>2</sub> interface. The fit indicates a time scale for hole-pair recombination of about 1 ns. (b) Calculated shift in XPS peak position vs number of electrons transferred to the TiO<sub>2</sub> for AuNPs with different radii ( $R_{sp}$ ).

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