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S E M I N A R
aus
Halbleiterphysik und Nanotechnologie

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Plasmonic Nanoreactors: From Fundamentals to Applications

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Our understanding of the exact physical mechanism behind plasmon-induced photocatalysis is far from complete despite this being one of the most active research topics in plasmonic applications[1]. In particular, the role of localized temperature remains a controversial question[2–4]. In this seminar to the Semiconductors and Nanotechnology series, we will discuss critical insights at the nanoscale that show plasmon-induced photocatalytic activity and the role of localized heating. To do this, we use 4-nitrobenzenethiol (4NBT) self-assembled monolayers formed on plasmonic nanostructures as a benchmark model of photocatalytic activity investigated by surface- and tip-enhanced Raman spectroscopy (SERS and TERS). We will see how SERS results show that an external temperature increase promotes the photocatalytic conversion of 4NBT to azobenzene products in agreement with Arrhenius law. However, our TERS imaging results at the single nanoparticle level show that regions with the highest catalytic conversion do not correlate with regions having the largest electromagnetic field enhancement. We attribute this mismatch between photocatalytic activity and enhancement to a competition between these two processes in terms of energy conservation. These results imply that the hot-electron transfer is not the only contributor to these kinds of reactions but that the non-radiative plasmon decay into thermal energy does play a critical role. This work impacts other applications such as theranostics based on photothermal therapy and plasmonic signal enhancement since these two functions cannot be simultaneously amplified in single-nanoparticle systems. We will end up with a brief discussion of the applications of these new insights in flexible electronics and sensors for biomedical applications[5].

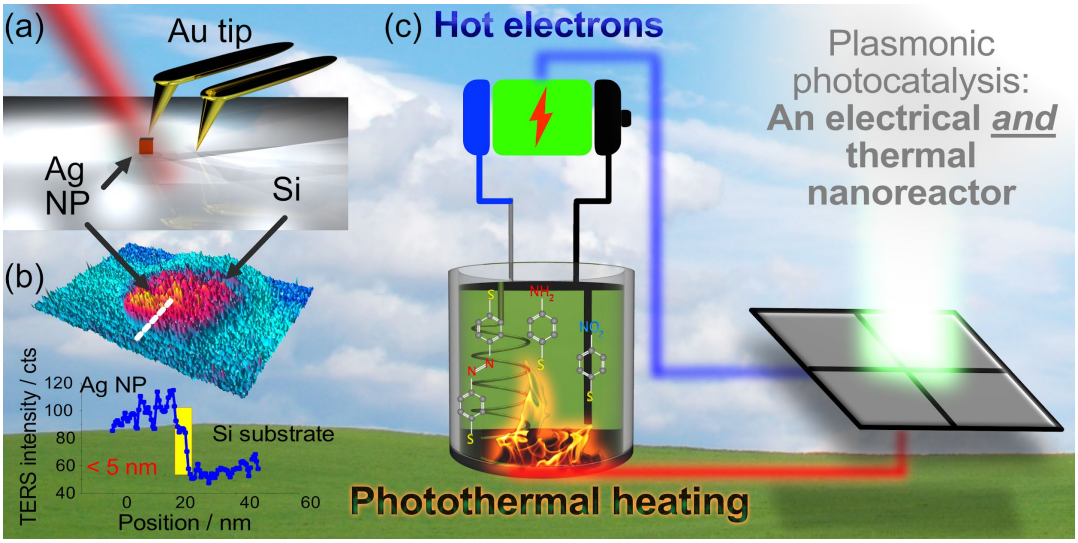

Fig. 1 (a) Sketch of the Au tip on a 4NBT-functionalized surface with the TERS nanoscale imaging result in (b). The ultimate application of plasmonic photocatalysis is to harvest sunlight to drive chemical processes as well as sensing applications that are now emerging. We will discuss how thermal and electronic contributions play fundamental roles in plasmon-driven reactions investigated by SERS and TERS.

References

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(2) Un, I.-W.; Sivan, Y. The Role of Heat Generation and Fluid Flow in Plasmon-Enhanced Reduction–oxidation Reactions. *ACS Photonics* **2021**, *8* (4), 1183–1190.
(3) Ultrafast Nanoscale Raman Thermometry Proves Heating Is Not a Primary Mechanism for Plasmon-Driven Photocatalysis. https://doi.org/10.1021/acsnano.8b01809.s001.
(4) Golubev, A. A.; Khlebtsov, B. N.; Rodriguez, R. D.; Chen, Y.; Zahn, D. R. T. Plasmonic Heating Plays a Dominant Role in the Plasmon-Induced Photocatalytic Reduction of 4-Nitrobenzenethiol. *The Journal of Physical Chemistry C*. 2018, pp 5657–5663. https://doi.org/10.1021/acs.jpcc.7b12101.
(5) Rodriguez, R. D.; Shchadenko, S.; Murastov, G.; Lipovka, A.; Fatkullin, M.; Petrov, I.; Tran, T.; Khalelov, A.; Saqib, M.; Villa, N. E.; Bogoslovskiy, V.; Wang, Y.; Hu, C.; Zinovyev, A.; Sheng, W.; Chen, J.; Amin, I.; Sheremet, E. Ultra-Robust Flexible Electronics by Laser-Driven Polymer-Nanomaterials Integration. *Advanced Functional Materials*. 2021, p 2008818. https://doi.org/10.1002/adfm.202008818.