Localized plasmonic catalysis by SERS and TERS

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With the help of plasmon-induced hot electrons, plasmonic catalysis was recently designed as a new exciting topic of heterogeneous catalytic reaction. Our recent research indicates that plasmonic catalysis opens a route to concentrate and direct the energy of visible light to adsorbed molecules, hence, enhancing the rate of chemical reactions and offering a pathway to control reaction selectivity. The plasmonic catalysis of dimerization of p-nitrothiophenol (pNTP) was observed by surface enhanced Raman scattering (SERS) in 2011. As shown in Fig. 1, we report on a new plasmon catalyzed cleavage reaction of pNTP at a single molecule (SM) level using a gold nanoparticle dimer to avoid the usual dimerization [1]. Our newest experiments indicate that TP molecules can also react to oNTP and pNTP by SERS. Tip-enhanced Raman scattering (TERS) is a technique that provides molecular information at the nanoscale. As shown in Fig. 2, a controlled plasmonic catalysis of dimerization of pNTP was monitored by AFM and STM TERS [2]. Especially, the temperature of plasmonic catalysis can be obtained by comparing stokes and anti-Stokes TERS directly at the site of interest.
In addition to the above mentioned reactions, already more reactions based on plasmonic catalysis such as the dissociation of DMAB and bond-selective dissociation of malachite green molecules were investigated by using TERS and will be discussed [3].

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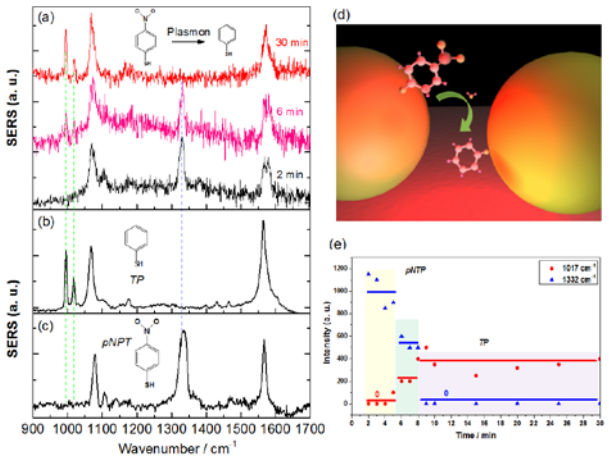

Fig. 1: *Comparison of time dependent SERS spectra of pNTP* ***(a)*** *and a comparison to reference spectra of TP* ***(b)*** *and pNTP* ***(c)****, reaction scheme* ***(d)*** *and time dependent track on a single molecule level* ***(e)****.*

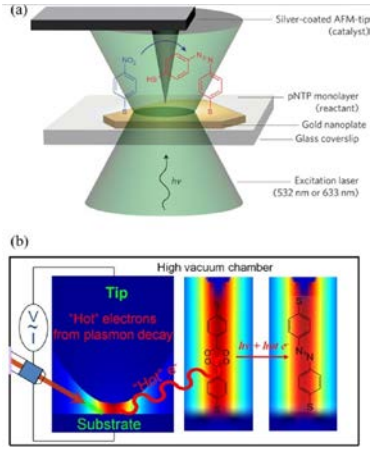

Fig. 2: *Schematic of the plasmon catalyzed dimerisation of pNTP by (a) AFM-TERS and (b) STM-TERS.*

[1] Z. Zhang et al., Chem Comm, 2015, DOI: 10.1039/C4CC09008J.
[2] E. M. van Schrojenstein Lantman, et al., Nat Nanotechnol, 2012, 7, 583-586; M. T. Sun, et al., Sci Rep, 2012, 2, 647.
[3] Z. Zhang et al. Nanoscale, 2013, 5, 3249-3252; Z. Zhang et al. Nanoscale, 2014, 6, 4903-4908.