

vary, affecting the local free-charge distribution around the object. The local free-charge distribution must satisfy Gauss's law and can be controlled by an applied a.c. field, conserving the total amount of charge. This interdependent set of forces creates a flow of charges (electro-thermo-plasmonic flow) that imposes a net body force on the object, which is consequently pushed towards the Au nanodisks. The electrothermoplasmonic tweezers can attract 300-nm-diameter spheres towards the gold nanodisk from a large distance (up to about 100  $\mu\text{m}$ ).

Another advantage of these nanotweezers is the much larger radius of action compared with earlier plasmonic tweezers. In the latter system, the operator has to wait for the trapped object to diffuse through the active area where the radiation pressure generates the potential needed for optical manipulation. This area is usually limited to the plasmonic hot spot and usually is no larger than a few nanometres squared.

The electrothermoplasmonic tweezers instead operate in a complete non-contact mode and with their 'long arm' can pick up objects that lie much farther away, while maintaining nanometre resolution during manipulation. Indeed, the flow speed can reach more than 40  $\mu\text{m s}^{-1}$ , depending on the initial position of the bead relative to the gold nanodisk, the laser power, and the a.c. power. As an example, Boltasseva and co-workers demonstrate that they can position 300-nm-diameter beads at will by modulating the a.c. field power and then switching it off (Fig. 1b). The flow speed drops to 75  $\text{nm s}^{-1}$  when the a.c. field is turned off, essentially stopping the motion of the bead.

These electrothermoplasmonic tweezers have the potential to be used with molecular systems too, as they are based on mass flow and there are no intrinsic limitations on how small the trapped object can be. An exciting development would be to promote chemical reactions by transporting

reactants to specific locations of a metallic surface and exploiting the photocatalytic properties of surface plasmons. Based on these advantages, electrothermoplasmonic tweezers will certainly stimulate further studies and extend the realm of applications well beyond the medical sciences.  $\square$

Yasuyuki Tsuboi is at the School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan.

e-mail: [twoboys@sci.osaka-cu.ac.jp](mailto:twoboys@sci.osaka-cu.ac.jp)

#### References

1. Ashkin, A. *Phys. Rev. Lett.* **24**, 156–159 (1970).
2. Bustamante, C., Bryant, Z. & Smith, S. *Nature* **421**, 423–427 (2003).
3. Righini, M. & Quidant, R. *et al. Phys. Rev. Lett.* **100**, 186804 (2008).
4. Grigorenko, A. N. *et al. Nature Photon.* **2**, 365–370 (2008).
5. Ndukaife, J. C. *et al. Nature Nanotech.* **11**, 53–59 (2016).
6. Shoji, T. & Tsuboi, Y. *Phys. Chem. Lett.* **5**, 2957–2967 (2014).
7. Berthelot, J. *et al. Nature Nanotech.* **9**, 295–299 (2014).
8. Tsai, W., Huang, J.-S. & Huang, C. *Nano Lett.* **14**, 547–552 (2014).
9. Roxworthy, B. J., Bhuiya, A. M., Vanka, S. P. & Toussaint, K. C. Jr *Nature Commun.* **5**, 3173 (2014).

Published online: 2 November 2015

## NANOREACTORS

# Chemistry in and out of nanoflasks

The light-powered assembly and disassembly of functionalized nanoparticles creates dynamic nanocavities with built-in selective uptake, reactivity and release.

Stefan Hecht

Nature has evolved enzymes to carry out chemical transformations with high efficiency and selectivity, in specific locations and at defined times. Chemists not only uncovered the underlying concept that confinement is crucial for the remarkable success of enzymatic reactions, but also developed ways to concentrate reactants inside compartments to achieve dramatic rate accelerations and spatial preorganization of molecules for improved selectivity. To exploit the advantages of confinement, the dimensions of the compartment as well as the chemical decoration of its inner walls need to be controlled. A large variety of materials with engineered pores, such as zeolites, silicates, organic frameworks and molecularly imprinted polymers, have been reported in recent years. Despite significant progress in the field, a major drawback of these porous materials lies in the necessity for reactants to diffuse in and (even more importantly) for products to diffuse out, both of which are usually slow processes. Writing in

*Nature Nanotechnology*, Rafal Klajn and co-workers at the Weizmann Institute of Science in Israel and the University of Illinois at Chicago now report a clever and conceptually different approach to overcome this limitation<sup>1</sup>, in which light is used to assemble and disassemble nanoparticles, thereby creating dynamic nanoflasks.

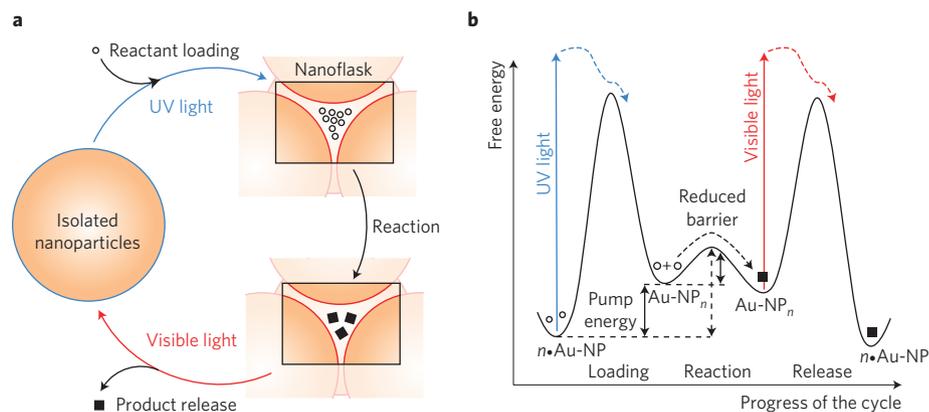
Previous observations had shown that gold nanoparticles functionalized with azobenzene photoswitches can undergo light-induced self-assembly<sup>2,3</sup>. The driving force behind this aggregation process is the photoinduced formation of *Z*-azobenzene at the nanoparticle surfaces, which leads to the entropically favoured release of nonpolar solvent molecules. By packing nanoparticles measuring a few nanometres in diameter, most favourably in a hexagonally close-packed lattice, nanosized gaps remain in between each of five neighbouring particles, thereby effectively creating a nanoflask. The inner voids of the aggregates are ideally suited for use as tiny reaction vessels because they provide both sufficient

space and specific interactions between the molecules and the nanoflask walls. By changing both the dimension (and hence the surface-to-volume ratio) and surface decoration of the nanoparticles, the researchers were able to quantify the uptake and control the reactivity of small guest molecules inside the nanoflasks. Additionally, by introducing chiral moieties on the surface of the nanoparticles, they achieved enantioselective accumulation of chiral guest molecules.

Klajn and colleagues demonstrated the usefulness of their approach by monitoring the outcome of two chemical reactions: the hydrolysis of an acetal and a photochemical anthracene dimerization, in the absence and presence of their nanoflasks. Alternating ultraviolet and visible light exposure caused the system to undergo cycles of nanoparticle assembly and disassembly. Under these conditions, both reactions proceeded either only or at least faster within the nanoflasks, with the anthracene dimerization exhibiting strongly altered regioselectivity. The

origin of the observed rate acceleration is due to an increased local concentration inside the nanoflasks and an effectively reduced energy barrier, which arises from ‘pumping’ the system to metastable Z-azobenzene-containing aggregates (Fig. 1).

This work is conceptually different from earlier approaches, which attempted to gate access to porous materials by attaching photoswitchable units to static structures, such as in the case of zeolites<sup>4</sup> or organic frameworks<sup>5</sup>. The main intrinsic advantage of the work of Klajn and colleagues lies in the significantly higher speed at which the reactants get trapped inside and the products released from the cavities. The generality of this approach is also a key advantage, as control over chemical reactions does not rely on modifying a specific catalyst, but rather on engineering the dimensions and surface chemistry of the vessel. To exploit these unique features fully, the rates of the assembly and disassembly process must be optimized with regard to the rate of chemical transformation (Fig. 1). However, this also implies that the system requires several photoinduced switching events, which would consume many photons during the various assembly and disassembly cycles. Future work should focus on optimizing the energy efficiency of the approach, which requires a constant input of energy (a general feature of far-from-equilibrium systems<sup>6</sup>), by minimizing the amount of azobenzene needed to induce assembly and disassembly. Furthermore, the system should be integrated into a continuous chemical process that involves ideally thermal (rather



**Figure 1** | Dynamic nanoflasks. **a, b**, Ultraviolet light induces the aggregation of gold nanoparticles ( $n\bullet\text{Au-NP}$ ; denoting  $n$  free gold nanoparticles in solution) functionalized with azobenzene photoswitches (*E* isomers, blue outer layer; *Z* isomers, red outer layer) and (chiral) recognition units, leading to the formation of tiny reaction vessels ( $\text{Au-NP}_n$ ; gold nanoparticle aggregate consisting of  $n$  gold nanoparticles,  $n\bullet\text{Au-NP}$ ) of controlled size and specific surface chemistry. The nanoflask concentrates reactants (open circles) and thus accelerates conversion to products (filled squares) with enhanced stereoselectivity. Visible light is then used to disassemble the nanoflasks and release the products (**a**). Alternating illumination with ultraviolet and visible light therefore drives a dynamic exchange of chemicals and powers a catalytic cycle, as detailed in a qualitative potential-energy landscape (**b**).

than photochemical) bimolecular reactions, as in the case of a dynamic kinetic resolution or a polymerization reaction. In the latter case, the nanoflask might enable control over the molecular weight distribution of the final polymer. Finally, activity and bias selectivity could be further improved by attaching specific molecular catalyst units to the nanoparticles. □

Stefan Hecht is in the Department of Chemistry and Integrative Research Institute of the Sciences

(IRIS) Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany. e-mail: [sh@chemie.hu-berlin.de](mailto:sh@chemie.hu-berlin.de)

#### References

1. Zhao, H. *et al.* *Nature Nanotech.* **11**, 82–88 (2016).
2. Klajn, R., Bishop, K. J. M. & Grzybowski, B. A. *Proc. Natl Acad. Sci. USA* **104**, 10305–10309 (2007).
3. Manna, A. *et al.* *Chem. Mater.* **15**, 20–28 (2003).
4. Ferris, D. P. *et al.* *J. Am. Chem. Soc.* **131**, 1686–1688 (2009).
5. Heinke, L. *et al.* *ACS Nano* **8**, 1463–1467 (2014).
6. Mattia, E. & Otto, S. *Nature Nanotech.* **10**, 111–119 (2015).

Published online: 23 November 2015

## 2D MATERIALS

# Single photons at room temperature

The observation of single-photon emission at room temperature from defects in hexagonal boron nitride sheets opens new opportunities for quantum optics.

Jörg Wrachtrup

When light is emitted from a source embedded in a solid-state device, most of the emission gets trapped within the solid itself yielding poor emission efficiency. This is an obstacle for the realization of quantum optics devices. To avoid this trapping, an easy solution is to use light sources embedded in 2D materials, which in addition offer other advantages over bulk solid-state devices.

For example, the space confinement of negative and positive carriers (electrons and holes, respectively) is relatively high in 2D crystals, and can be further enhanced by gate electrodes. Quantum light emission from defects in 2D crystals has recently been reported from groups studying semiconducting dichalcogenides. Now, writing in *Nature Nanotechnology*, Igor Aharonovich and colleagues from

the University of Technology Sydney report single-photon emission up to room temperature from single defects in hexagonal boron nitride (hBN) nanoflakes<sup>1</sup>.

The optical properties of 2D materials have been studied extensively since the discovery of 2D semiconducting transition-metal dichalcogenides (TMDs). Recently, single-photon emission from layers of the semiconducting TMD  $\text{WSe}_2$  has been