semitransparent perovskite on top of a interdigitated back-contacted silicon solar cell. Earlier this year, it reported devices that operate with an efficiency of 20.2% for a cell area of 4 cm^2 and 17.2% for larger areas up to 16 cm^2. Importantly, at PSCO, IMEC with its partners in Germany ZSW and Karlsruhe Institute of Technology announced its latest results with CIGS — a stacked, semitransparent perovskite on CIGS tandem solar cell module with an efficiency of 17.8% and an area of 3.8 cm^2 (go.nature.com/2fd1TXw).

Other groups are investigating combining perovskites with different material systems. For example, Hiroshi Segawa from the University of Tokyo discussed the opportunities for combining perosvkite with wideband dye-sensitized solar cells in a hybrid approach. Working with the École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland and groups in South Korea they have made a hybrid cell based on a dye-sensitized solar cell with a long-wavelength dye called DX3 that absorbs up to 1,100 nm in the near-infrared and a perovskite cell to achieve an efficiency of 21.5%. The design uses a dichroic mirror to split sunlight into its infrared and visible constituents that are directed towards the dye-sensitized solar cell and the perovskite cell, respectively.

In addition, other teams are performing detailed modelling and simulations to uncover the efficiency limits of perovskite/silicon tandem designs. For example, Moritz Futscher from FOM-AMOLF in the Netherlands told delegates that the climatic conditions change the optimum design of the tandem cells and that devices optimized for use in the US and Europe would be different. While Dale Grant from the Australian National University has been modelling the optical losses in tandem designs and says that a key challenge is to reduce reflections at internal interfaces due to refractive index mismatches and that there is a need to find high-index electron- and hole-transporting materials.

One aspect that several talks highlighted is that there are different ways of 'wiring up' tandem cells and that this needs to be carefully considered. Each subcell can be wired up and operated independently in a so-called four-terminal (4T) design (that is, two electrodes for each subcell). This has the advantage that each subcell can be independently optimized, however, it adds additional complexity of double the number of electrical connections and also necessitates twice the number of electrical invertors for dealing with the output from the cells. Alternatively, the output from the two subcells can be combined and thus just two electrodes can be used as in a single-junction cell (2T design), but this introduces the need to current match the output from the subcells, which can be difficult. At present, the 4T designs display the highest efficiencies, but it is not yet clear which design is the most practical commercial solution.

It seemed fitting then, that the very last talk of the conference was on the topic of high-efficiency 4T tandem cells, with Bjoern Niesen reporting work carried out at the EPFL and the Centre Suisse d'Electronique et de Microtechnique (CSEM) in Switzerland. Their research group has recently published results for a 4T perovskite/silicon tandem cell with an efficiency of 25.2% (J. Werner *et al.*, *ACS Energy Lett.* **1,** 474–480; 2016). He said that improvements in this figure could be achieved by reducing parasitic absorption losses in the hole-transport layer and buffer layers of the cells.

The next PSCO conference will take place in Oxford, UK in autumn 2017. ❐

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SINGLE-PARTICLE SPECTROSCOPY

Whispers of absorption

The combination of whispering-gallery-mode sensing with photothermal absorption spectroscopy promises significant advances in single-molecule identification.

Matthew R. Foreman

Recent decades have seen an explosion of interest in the detection and spectroscopy of single molecules. Traditional experimental techniques perform measurements on large collections of molecules such that only average properties can be determined. By contrast, through the analysis of individual molecules — be they fluorescent dyes, polymer chains, proteins or even single ions — complex physical, chemical and biological systems can be studied in minute detail. The vastly richer knowledge offered by such single-molecule techniques has had far-reaching implications in fields as diverse as quantum optics, biophysics and analytical chemistry. For example, observations of DNA transcription, antigen recognition and protein unfolding at the level of individual molecules have provided great insight into the complex mechanisms governing life[1].

Most early single-molecule experiments monitored light emitted from fluorescent molecules. These powerful and still widespread approaches typically require labelling of the target molecule with suitable dye molecules to generate a detectable signal. However, labelling comes at a cost: it not only requires a complicated modification protocol to incorporate the fluorophore into the target molecule, but it can also critically affect molecular function[2], which is itself often the subject of research interest. To overcome these issues, a number of label-free detection methods have been developed[3]. Writing in *Nature Photonics*, Heylman and collaborators now report the detection and spectroscopic characterization of metallic nanoparticles with a technique that achieves very high detection sensitivity without the need for fluorescent labels[4].

A leading label-free detection method is based on optical microcavities, the simplest example being that of two highly reflecting planar interfaces. In such cavities, light is 'trapped' within the intermediate space between the interfaces through multiple reflections. Similarly, electromagnetic waves can be confined to closed circular paths, known as whispering gallery modes (WGMs), within spherical, toroidal or other rotationally symmetric resonators. The refractive index of a WGM resonator is larger than that of the surrounding medium, such that light propagates around the inner surface of the resonator through successive total internal reflections. As a result of light

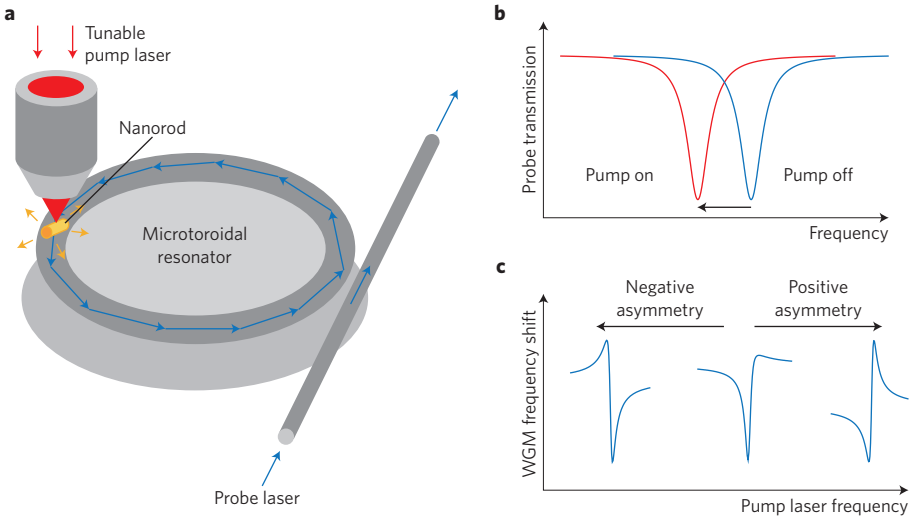

Figure 1 | Absorption spectroscopy of plasmonic nanoparticles using a microtoroidal whispering gallery mode (WGM) resonator. **a**, Using a pump–probe beam arrangement, a plasmonic nanorod is resonantly illuminated causing the nearby microcavity to heat up. **b**, Due to the photothermal effect, the temperature change in the resonator causes its resonance frequency to shift. **c**, The measurement of the WGM frequency shift as a function of the pump laser frequency gives access to an absorption spectrum that exhibits several Fano resonances originating from WGM–nanoparticle interactions and characterized by different asymmetries in distinct spectral regions. Figure adapted from ref. 4, Nature Publishing Group.

interference after each cavity round trip, only specific wavelengths are significantly confined, that is, resonant with the cavity. The resonance wavelengths are dictated by the refractive index of both the cavity and its host medium; the latter dependence derives from the evanescent wave generated in the host medium as a result of total internal reflection. As a consequence, when a particle of interest adheres to the resonator surface it modifies the effective refractive index experienced by the WGM, which in turn induces a measurable shift in the WGM resonance frequency: this is the basic transduction mechanism used in many WGM sensors[5].

Albeit extremely sensitive, WGM sensors lack the ability to discriminate between different types of particle. This functionality is a crucial requirement for the analysis of heterogeneous samples such as blood, and in applications such as environmental monitoring or clinical diagnostics where discrimination between toxins or pathogens and otherwise harmless molecules is of paramount importance. Fluorescence-based techniques can avoid this issue by building a chemical specificity into the labelling stage, whereas the surface of WGM sensors can be chemically modified so that only desired target molecules can bind to it. Nevertheless, both strategies are limited in the range and number of particles that can be identified in any given measurement. Enter spectroscopy, which is a powerful route to molecular identification since molecules possess complex and unique spectral fingerprints. Surface-enhanced Raman spectroscopy, for example, is well known in plasmonics and can be realized on a WGM platform thanks to the strong surface fields associated with WGMs[6]. The alternative approach explored by Heylman and co-workers demonstrates that a WGM microtoroidal resonator can be used as an absorption spectrometer. Combining the principles of photothermal spectroscopy and WGM sensing, the authors acquired absorption spectra of metallic nanoparticles with high detection sensitivity, thus taking the first step towards label-free single-molecule identification on a WGM platform.

The photothermal effect is a phenomenon whereby the energy of light absorbed by a material or molecule is dissipated as heat, causing a corresponding temperature increase ΔT in the material. As a consequence, the refractive index of the medium is also modified according to $\Delta n = \alpha \Delta T$, where α is the thermo-optic coefficient. Heylman and collaborators use a tunable pump laser spanning wavelengths between 1,280 and 1,370 nm, which they tightly focus onto a rod-like gold nanoparticle adsorbed to the surface of small silica toroidal resonators of major radius ~23 μm and characterized by optical quality factors up to 10^7 and mode volumes ~300 μm^3 (Fig. 1a). As a result, conduction electrons in the metallic nanorod are excited into oscillation. By choosing the dimensions of the nanorod correctly (250 nm in length and 25 nm in diameter, in this case), the natural frequency of these oscillations — or localized plasmons — can be matched to that of the pump laser such that the oscillations are driven resonantly and the amount of energy absorbed by the material increases. Ohmic losses, however, cause the energy stored in the localized plasmons to be dissipated as heat, warming up the nanorod. Through thermal conduction, the heat produced is also transferred to the nearby resonator: this in turn implies that its temperature, refractive index and ultimately its resonance frequency change (Fig. 1b). If the power of the pump laser varies periodically, the thermal signal corresponding to the induced WGM resonance shift also oscillates at a given modulation frequency (here ~2 or ~4 kHz). A lock-in amplifier operating at this frequency allows the team to monitor the variations of the WGM resonance while mitigating noise to ensure sensitive measurements. The sensitive read-out of the toroid resonance frequency is based on an additional probe laser, which is actively locked to a WGM resonance in a feedback loop using the Pound–Drever–Hall technique. More specifically, locking is realized through phase modulation of the probe laser at a high frequency of 200 MHz. The subsequent measurement of the transmitted photocurrent mixed with a known reference beam (or local oscillator) provides an error signal for the feedback loop that is proportional to the derivative of the WGM resonance lineshape. This error signal makes it possible to tune the probe laser back into resonance with the toroid, and at the same time act as a direct measure of any WGM frequency shift that occurs. The authors stress that it is this double modulation scheme that is responsible for detection sensitivity well beyond current state-of-the-art WGM sensors. Indeed, Heylman and co-workers experimentally determine the limit of detection for their system — an important metric quantifying the smallest measurable WGM resonance shift. For this purpose, they systematically reduce the power of the pump beam to decrease the absolute energy absorbed by the plasmonic nanoparticle, and find that they can measure a resonance frequency shift as small as ~84 Hz, which is equivalent to a change in the resonator's temperature of about 100 nK or to a thermal power close to 10^{-11} W. This impressive detection limit is approximately three orders of magnitude below the thermal power emitted by a single

dye molecule[7]. More accurate quantitative spectral measurements would require an extension of the present thermal model to include additional effects such as the expansion of the resonator and temperature changes in the host medium. Nonetheless, the current results suggest that application of the team's technique to single molecules, as opposed to plasmonic particles, might not be too far off.

Although the demonstration carried out by Heylman and co-workers is restricted to plasmonic absorbers, it exemplifies the possibilities that absorption spectroscopy can afford. Use of plasmonic nanoparticles has attracted attention in WGM sensing, but only as a means to enhance the local field and thus detect ever-smaller particles[5,8]. Moving beyond this paradigm, the authors have experimentally studied the physical interaction between very narrow WGM resonances and relatively broad plasmonic resonances for the first time. To support their experimental observations, Heylman and colleagues used a coupled-oscillator model to describe the WGM–nanoparticle interaction. Their theoretical analysis shows that the large difference in the widths of the WGM and plasmonic resonances implies that the interference between WGMs and plasmonic modes produces a characteristic asymmetric spectral lineshape (Fig. 1c) known as a Fano resonance[9]. The spectral profile of this Fano resonance depends on the difference between the WGM and plasmonic resonance frequencies because this quantity dictates the relative phase between the modes. As toroidal resonators support many WGMs at different wavelengths, each of which interacts with the plasmon oscillation, one should expect a dense 'forest' of Fano resonances to appear. Indeed, the existence of a set of Fano resonances is experimentally observed by Heylman and collaborators, whose data further indicate that the asymmetry of the Fano resonances varies across the measured absorption spectrum. These results support the coupled-oscillator model adopted in this as well as in previous theoretical studies.

Single-molecule detection has proved pivotal in many branches of science. The work of Heylman and colleagues highlights the potential analytical capabilities of single-molecule WGM measurements, which allow for highly sensitive spectral analysis of individual unlabelled molecules. This capability can be expected to facilitate the development of on-chip single-molecule identification technology for clinical, environmental and several other applications. Therefore, these whispers of absorption are just the beginning of a promising scientific conversation. ❐

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