Monitoring Morphological Changes in 2D Monolayer Semiconductors Using Atom-Thick Plasmonic Nanocavities

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ABSTRACT Nanometer-sized gaps between plasmonically coupled adjacent metal nanoparticles enclose extremely localized optical fields, which are strongly enhanced. This enables the dynamic investigation of nanoscopic amounts of material in the gap using optical interrogation. Here we use impinging light to directly tune the optical resonances inside the plasmonic nanocavity formed between single gold nanoparticles and a gold surface, filled with only yoctograms of semiconductor. The gold faces are separated by either monolayers of molybdenum disulfide (MoS2) or two-unit-cell thick cadmium selenide (CdSe) nanoplatelets. This extreme confinement produces modes with 100-fold compressed wavelength, which are exquisitely sensitive to morphology. Infrared scattering spectroscopy reveals how such nanoparticle-on-mirror modes directly trace atomic-scale changes in real time. Instabilities observed in the facets are crucial for applications such as heat-assisted magnetic recording that demand long-lifetime nanoscale plasmonic structures, but the spectral sensitivity also allows directly tracking photochemical reactions in these 2-dimensional solids.

KEYWORDS: tunable plasmons, 2D-materials, molybdenum disulfide, waveguides, nanoparticles, nano-optics

The nanoparticle on mirror (NPoM) geometry provides unique possibilities to study isolated plasmonic junctions reliably and over a long time. In contrast to individual nanoparticle (NP) dimers, this geometry allows for simple placement of ultrathin spacer materials into the gap and hence to create stable and well-defined junctions with intriguing materials properties (Figure 1a). Since the discovery of graphene and a range of other 2-dimensional (2D) materials, combining them with plasmonics is of growing interest for a wide range of applications in nano-optoelectronics, quantum information, and biosensing.

The optical scattering spectrum of a NP near a metallic surface consists of several coupled modes. In the work here, the combination of ultrathin gaps and faceting of the NPs produces nanometer-thick plasmonic cavities in which resonant gap plasmons are confined to form lateral standing waves (of mode index \( s = 1, 2, 3, \ldots \)). The spectral positions of these modes reveal the morphology of the nanostructure and are highly sensitive to small variations of the NP facet sizes. We demonstrate that both semiconductor gap composition and NP morphology can be changed by optical irradiation, thus actively tuning the coupled plasmons as well as tracking few-atom restructurings.

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oxide which enables direct real-time study of the far-field response to variations of the dielectric environment inside the gap.

Surface-enhanced Raman scattering (SERS)\textsuperscript{11,16–20} confirms that all studied AuNPs sit on top of these semiconductor layers (see Supporting Information), which are immersed in the intense enhanced optical fields from the coupled plasmons. Raman scattering from MoS\textsubscript{2}-filled gaps is enhanced by >5 orders of magnitude (Supporting Information Figure S2) when resonantly excited at 633 nm while the photoluminescence remains unaffected (Supporting Information Figure S2c).

The dark-field scattering spectra of individual NPoMs exhibit four clear modes (Figure 1e), which match those expected from full electromagnetic simulations (Figure 1f). Using a supercontinuum source and infrared reflecting objective (Methods), we access the spectral range up to 1700 nm. The short-wavelength \( T \) mode is accompanied by gap-plasmon modes labeled \( j_{1,2,3} \) which theory shows match the lateral standing wave symmetries. Irradiating the NPoM at high angles (using high-NA objectives) accesses the vertical field polarizations of these gap plasmons.\textsuperscript{7} We clearly resolve the more dipole-like mode in the infrared which has a broad line shape because it is radially well-coupled. The plasmonic nature of these modes is confirmed by polarization-resolved measurements (Supporting Information Figure S3). Because of the higher noise for \( \lambda > 1000 \) nm arising from the smaller collection NA and detection efficiency, for the rest of this paper we concentrate on the \( j_{2,3} \) modes in the visible/near-IR and employ dark-field refracting objectives.

The NPoM forms a metal–insulator–metal cavity with lateral boundary conditions defined by the facet width (Figure 1c, Figure 2a,b)\textsuperscript{21–23} The basis states in this cavity for in-plane wavevector \( k_{\|} \) correspond to the MIM waveguide dispersion \( E(k_{\|}) \), which can be calculated for very thin gaps\textsuperscript{24,25} (\( d < 10 \) nm) giving the effective waveguide refractive index, \( n_{\text{eff}} = hck/E \) (see Supporting Information eq S1, Figure S8), dependent on the dielectric constants \( \varepsilon_{m} \) in the metal and \( \varepsilon_{d} \) the gap dielectric. The facet width defines lateral discretization of these MIM waveguide modes resulting in solutions of different symmetry within the cavities. In a 1D depiction, the \( s \) modes resemble standing waves (Figure 2), as discussed below. For the 2D modes on a circular drum-like facet, this gives approximate solutions for the resonant incident wavelengths \( \lambda_{s} = \pi n w / \alpha_{s} \), where \( w \) is the facet diameter, \( \alpha_{s} = \alpha_{1} + \phi_{s} \), and \( \phi_{s} = 3.8, 7.0, 10.2, ... \) is the \( i \)-th antinode of the \( \lambda_{0} \) Bessel function, while \( \phi_{s} \) is a phase-shift extracted from the exact simulations.\textsuperscript{26} The \( s = 1 \) mode (associated with \( \alpha_{1} \)) is suppressed in large cavities due to charge symmetry considerations (to be reported elsewhere). An even simpler analytic expression
The sensitivity of this nanomaterial construct to irradiation depends on using the pinhole-free ultrathin semiconductor as structural barriers preventing fusion of the AuNPs and Au substrate. Irradiation excites electrons both in the semiconductor layers and in the local gold surroundings. Since plasmon tunings observed here are irreversible, they do not arise from instantaneous changes in the semiconductor refractive index via electronic nonlinearities. Instead, irreversible changes in nanojunction geometry and composition occur through several mechanisms.

The slow red-shift of the plasmonic modes with irradiation can be explained by nanoscale resculpting of the gold atoms around the junction region. Effects of gold mobility have been observed previously for both intense optical and thermal excitation. Here, both nanoscale optical forces and opto-thermal heating induce a restructuring at the gap, although no global morphology change is apparent in SEMs (despite strenuous efforts because they are so small changes, see Supporting Information). The gap plasmons in the MIM cavity formed by the semiconductor spacer red-shift as the lower NP facet grows (inset Figure 3a), which happens as mobile Au surface atoms are dragged into this ultrathin “optical capacitor” (Figure 3c). We find that no other explanations are capable of accounting for
the spectral changes observed, given that the gap material remains intact (see below). For instance alternative tuning effects could arise from local damage of the MoS2 spacer. This can be ruled out as the SERS and photoluminescence are not affected by optical irradiation, confirming that the integrity of this system is preserved while Au reconstruction takes place. Conducting pinholes would yield blueshifts by discharging the plasmonic gap, thus reducing the strength of the plasmonic coupling. Reorientation of the AuNP facet during irradiation is also unlikely as changes in the scattering would depend strongly on the exact gap morphology whereas the observed phenomena are highly reproducible over hundreds of investigated NPoMs.

With the use of eq 1, the rate of atoms arriving at the facet is

$$\frac{dN}{dt} = \frac{\pi a \lambda^2 i \lambda_j}{\lambda_p^2 - \lambda_j^2} \frac{d}{e^2} \frac{\lambda_j}{\lambda_p}$$

(2)

where the Drude plasma wavelength for Au is $\lambda_p = 154$ nm, and the atomic spacing $a = 0.4$ nm (see Supporting Information). This implies that a 1% shift in the $j_2$ mode corresponds to the arrival of 500 atoms onto the facet, or a change in facet radius of less than 1 atom. These light-induced plasmon shifts are investigated on a range of NPoMs with both MoS2 and CdSe nano-spacers (Figure 3d). The narrower gap formed by 0.7 nm MoS2 compared to 1.4 nm CdSe, as well as their different out-of-plane permittivities, produces longer wavelength gap modes for MoS2. This 40% additional red-shift corresponds to significantly greater field enhancement and localization inside the MoS2 2D semiconductor sheets. Similar red-shifts under UV irradiation are seen in all cases, with the spectral separation between $j_{2,3}$ always increasing. This is expected since confined MIM modes at higher energies sit where the dispersion is flatter (Supporting Information Figure S7) and thus tune less with a change in facet width. For the 30 nm-wide facets seen on most AuNPs here, the tuning rate of $\lambda_2$ is predicted to be 40% faster than $\lambda_3$ in line with our measurements. Irradiation with UV deposits energy predominantly in the gold as well as the semiconductor layers, concentrated near the gap by lightning rod effects. Irradiating with a 637 nm pump at identical power levels gives similar (but $\sim$10 times slower) red-shifts due to the reduced NPoM cross-section. While independent structural corroboration is inaccessible because these junctions are hidden beneath much bigger nanoparticles, we demonstrate here that optics provides an exquisitely sensitive tool to track material dynamics on the nanoscale. For the 1 nm spectral tracking of the plasmon modes available, we are already sensitive to $\sim$10 Au atoms adhering to the facets each 10 ms integration time, and this can be further optimized.

While neither the Raman scattering nor the photoluminescence from the MoS2-filled gaps are affected throughout the irradiation process, this is not true for the CdSe platelets. Simultaneous with the fast plasmonic red-shift seen at early times when irradiating the CdSe-filled gaps is a decay of the CdSe photoluminescence as well as a decay in the SERS strength of the longitudinal optical (LO) phonon (Figure 3b, Supporting Information Figure S5). Both decays happen on the same time scale and match the faster plasmonic redshift rate. However, the luminescence only decays down to $\sim$15% of its initial value regardless of illumination power suggesting that the CdSe is not ablated in the process.
METHODS

Sample Preparation. Flat gold layers 70 nm thick were electron-beam-evaporated onto Si wafers. For CdSe nanoplatelet monolayers, the gold surfaces were soaked in 5 mM aqueous 4-aminothiophenol (ATP) for 24 h. The surfaces were dipped in hexane solution with well-dispersed CdSe nanoplatelets for another 24 h. We obtain platelet monolayers with a surface coverage of ~60%. Single crystalline MoS$_2$ monolayers were grown by chemical vapor deposition (CVD) on a sapphire substrate. The MoS$_2$ monolayer is transferred to a gold substrate using a standard PMMA transfer method.

Experimental Spectroscopy. Optical spectroscopy was performed on a microscope in dark-field (DF) configuration connected to a CCD and using a confocal fiber collection arrangement coupled to a cooled spectrometer. A 100× dark-field objective (Olympus) with collection NA = 0.85 is used, providing excitation through an angular ring around 60° surrounding the collection cone. Intensities used were sufficiently low that no spectral changes were observed without additional laser irradiation. A pump laser (448 nm, 1 mW at sample) is coupled through the same microscope objective to study the irradiation dependence. The resulting power density on the sample is 140 kW/cm$^2$ given a measured spot size of ~3 mm. Control measurements were also carried out with a 637 nm laser with the same power density.

Infrared spectroscopy was performed using a Fianium SC-400 supercontinuum source with power density ~100 kW/cm$^2$ impinging from the side at an angle of 80° and a 40× reflective infrared objective with NA = 0.5 used for collection of scattered light.

Raman measurements were taken on a Renishaw InVia Raman microscope with resonant excitation of the plasmonic gap mode at 633 nm.

Dark-Field Scanning Transmission Microscopy (DF-STEM) Imaging. First, the NPoM was embedded in a platinum matrix which was evaporated onto the sample surface. A 500 nm thick cross-sectional slab was then isolated from the sample by focused-ion-beam milling, mounted on a TEM grid using a nanomanipulator and polished down to a thickness of ~100 nm. DF-STEM imaging was performed in a Hitachi S-5500 SEM at 30 kV acceleration voltage.

Theory Simulations. Exact simulations were carried out using the Boundary Element Method (BEM), with grids sufficiently small to ensure converged solutions in all cases. In the optical response of the NPoM, nonlocal effects are included in our local calculations by conveniently rescaling the separation distances and the dielectric function within the gap, as introduced in Teperik et al.$^{36}$ To that end, the combination of separation distance and dielectric function that best reproduces our experimental results is 0.6 nm for the gap distance and 3.24 for the transverse dielectric function of MoS$_2$, matching well the calculated values for monolayer MoS$_2$. This choice of parameters for the local calculations including nonlocal effects differs from the actual physical values by only a few Angstroms for the separation distance and a few tenths for the refractive index. A similar procedure was adopted for the CdSe layer.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This work was supported by the UK EPSRC grants EP/G060649/1, EP/L027151/1, Defence Science and Technology Laboratory (DSTL), and ERC grant 320503.
LINASS, C.T. and J.A. acknowledge financial support from Project FIS2013-41184-P from MINECO, ETORETEK 2014-15 of the Basque Department of Industry and IT756-13 from the Basque consolidated groups. Experiments were planned and carried out by D.O.S., J.M., L.O.H. and J.J.B. Nanoplatelets were synthesized by S.J. and B.D. MoS2 samples were fabricated by Y.S. and H.Y.Y. D.O.S., L.O.H., C.T., J.A. and J.J.B. carried out the simulations and developed the theory.

Supporting Information Available: Detailed discussion of the presented waveguide model as well as control experiments supporting the experimental results of this manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication: This paper published ASAP on December 17, 2014. Eq 2 was corrected and additional minor text corrections were made and the revised version was reposted on December 19, 2014.

REFERENCES AND NOTES


