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Micro-Extinction Spectroscopy (MExS): a versatile optical characterization technique

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Abstract

Micro-Extinction Spectroscopy (MExS), a flexible, optical, and spatial-scanning hyperspectral technique, has been developed and is described with examples. Software and hardware capabilities are described in detail, including transmission, reflectance, and scattering measurements. Each capability is demonstrated through a case study of nanomaterial characterization, i.e., transmission of transition metal dichalcogenides revealing transition energy and efficiency, reflectance of transition metal dichalcogenides grown on nontransparent substrates identifying the presence of monolayer following electrochemical ablation, and scattering to study single plasmonic nanoparticles and obtain values for the refractive index sensitivity and sensing figure of merit of over a hundred single particles with various shapes and sizes. With the growing integration of nanotechnology in many areas, MExS can be a powerful tool to both characterize and test nanomaterials.

Keywords: Hyperspectral imaging, Optical spectroscopy, Nanomaterial characterization, Transmission, Reflectance, Darkfield scattering, Two-dimensional materials, Transition metal dichalcogenides, Gold nanoparticles, Localized surface plasmon resonance

Background

The optical properties of nanoscale materials are exquisitely sensitive to their local structure, composition, and shape. Gold nanoparticles (NPs), for instance, can absorb green or red light, depending on their size [1]. Two-dimensional (2D) materials such as transition metal dichalcogenides (TMDs) sustain excitons that can be maneuvered in energy; their corresponding bandgaps vary as a function of thickness and composition [2]. While this sensitivity provides an exciting opportunity to tune light–matter interactions, it leads to large NP-to-NP and area-to-area variations and often results in heterogeneous broadening of the ensemble response. In these cases, reliable structure–property relationships can be obtained by performing spatially resolved optical spectroscopy, typically followed by structural characterization with electron or scanning probe microscopy [3].

Traditionally, spectroscopy relies on exciting a circular area of a sample with a focused probe, such as a laser or electron beam. The signal is then dispersed in energy and acquired on a camera that records intensity along the energy axis N_E . The probe can be scanned over the sample, along both x and y with a dwell time t , to yield a spectrum image of dimensions $N_x \times N_y \times N_E$ in txy units of time. This raster-scan approach to acquiring a hyperspectral datacube becomes prohibitively time consuming when considering large areas.

To overcome this limitation, several parallel acquisition schemes have been developed for optical spectroscopy, which have been reviewed elsewhere [4, 5]. One typical approach is the use of a tunable filter and a pixel array camera, enabling the acquisition of a range (albeit narrow) of wavelengths at a time; an $N_x \times N_y \times N_E$ datacube can then be acquired by scanning the filter's wavelength [6]. This comes at the cost of spectral resolution given the intrinsic wavelength spread (few nm) of the filter and the number of frames acquired. The acquisition time indeed scales as $t dE$, where dE is the energy step, and is ultimately indicative of the energy resolution. Another approach is the construction of a datacube by physically

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scanning the position of a spectrometer, acquiring one spectral dimension and one spatial dimension at a time (“push-broom”) enabling the acquisition of spectral information across the field of view. This allows for varied energy resolution, limited only by the spectrometer’s dispersion, and saves time by reducing the acquisition time to ty [7].

In this paper, we describe Micro-Extinction Spectroscopy (MExS), a novel optical characterization technique that can capture information regarding a variety of light–matter interactions in nanomaterials. In MExS, a LabVIEW interface orchestrates a piezoelectric sample stage, a spectrometer, and an electron-multiplied charge-coupled device (EMCCD) camera to acquire one lateral and one spectral dimension at a time, and then scans the other lateral dimension by moving the sample stage. Because it scans a line of pixels instead of a point, this approach greatly reduces the acquisition time, which scales as ty (line scan) rather than txy (point scan). This approach also allows for excellent spectral quality, and is therefore advantageous compared to creating datacubes via stacking energy-filtered images, which compromises spectral resolution. Finally, the size of the datacube is not limited by the field of view, but rather by the travel range of the (piezoelectric) stage. Many types of samples can be explored using MExS due to the various optical modes that MExS can support, including transmission, reflectance, and darkfield scattering. We have implemented these three optical capabilities, and describe a case study for each (“[Results and discussion](#)” section), demonstrating the applicability range of MExS.

Methods

Optical setup

The MExS setup (Fig. 1, and Additional file 1: Figure S1) consists of an inverted microscope system (Nikon Eclipse Ti), a piezoelectric stage (Physik Instrumente P-545.3C7), a spectrometer (Princeton Instruments IsoPlane SCT 320 equipped with a 50 grooves/mm grating), a 1024×1024 pixel array EMCCD camera (Princeton Instruments ProEM-HS: 1024BX3), an imaging camera (QImaging QIClick), a 12 V 100 W halogen lamp (Nikon D-LH/LC) for transmission and darkfield measurements, and an LED lamp (Lumen Dynamics X-Cite 120LED) for reflectance measurements. For scattering measurements, a dry darkfield condenser (Nikon, N.A. 0.95–0.80) is inserted in the optical path before the sample. The microscope is equipped with two objectives (Nikon CFI Plan Fluor 100XS Oil and Nikon CFI S Plan Fluor ELWD 40 \times) and an 80:20 beam splitter that sends 80% of the light to the spectrometer and 20% of the light to the imaging camera for simultaneous optical imaging and spectral measurements.

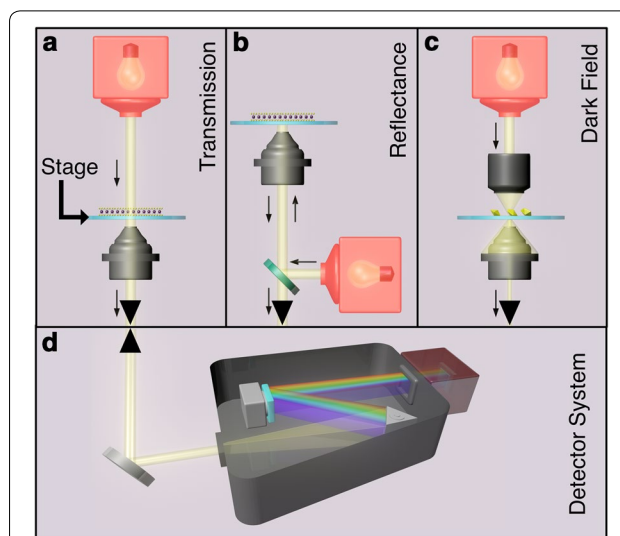


Fig. 1 MExS configurations. **a** Transmission configuration: light passes through the sample, and transmitted light is collected by the objective. This configuration provides information regarding the optical absorption properties of the sample. **b** Reflectance configuration: a half-mirror is used to direct light through the objective to the sample. The light that the sample reflects back is collected by the objective. This configuration enables the study of materials on nontransparent substrates. **c** Darkfield configuration: the darkfield condenser blocks direct signal from the light source resulting in the collection of only light scattered by the sample. This configuration allows for the study of small scattering structures such as plasmonic NPs. **d** Detector system: light that is collected by the objective goes through the spectrometer, and the intensity of dispersed light is recorded by the EMCCD

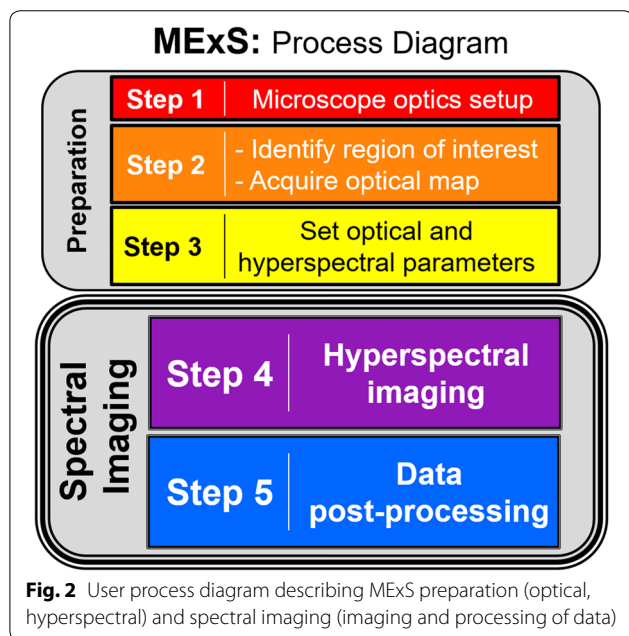
The dimensions of the acquired dataset depend on the spectrometer slit’s height and the stage’s range of motion (Table 1). The x dimension is defined by the slit height and scales with magnification (325 μm for the 40 \times , 140 μm for the 100 \times objective). The range of motion of the piezoelectric stage (here, 200 μm) defines the y dimension. The spatial resolution is diffraction limited, and the spectral resolution is defined by the choice of dispersion grating.

Hyperspectral data acquisition

Figure 2 shows the five steps involved when performing MExS. Prior to spectral imaging, the optical setup is constructed, and the sample is mounted onto the stage of the microscope. An image of the region of interest (ROI) is acquired using the imaging camera, creating a map used in data acquisition and analysis. The optical and hyperspectral parameters are then set; example parameters are shown in Table 2. Next, hyperspectral imaging is initiated, and data are exported in comma-separated value (CSV) files. Finally, experiment-specific post-processing calculations (Table 3) are performed on the data.

Table 1 Acquired dataset dimensions for various objective magnifications

Objective magnification	x dimension (slit-length limited), μm	y dimension (stage range-of-motion limited), μm
Acquired dataset dimensions		
100 \times	140	200
40 \times	325	200



The operation of this hyperspectral spatial-scanning technique relies on communication between two components: the sample stage and the detector system (Fig. 1). This communication is established and manipulated through a LabVIEW control (LabVIEW block diagram in Fig. 3a, LabVIEW user interface in Additional file 1: Figure S2). At the onset of the experiment, the LabVIEW code enters the “Initiate Software” mode. Once both software programs have been initiated and a line of communication has been established, the user enters the spatial-scanning hyperspectral parameters (step size, number of steps N_y) into the LabVIEW user interface. The user then advances the LabVIEW program into the “Acquire Data” mode; the detector and stage are manipulated in series to record data and move the sample N_y times. At each step, the detector system records 2D matrix with a spatial dimension (N_x) and a spectral dimension (N_λ), the lengths of which are defined by the EMCCD chip size, where $N_x=1024$ and $N_\lambda=1024$. An N_y stack of these 2D matrices creates an x - y - λ datacube (Fig. 3b). The piezoelectric stage used here employs a closed-loop system that records with high-precision the actual displacement of the stage, eliminating any significant concerns of hysteresis or stage drift on the measurement timescale. All scanning is done in the y -dimension.

MEaS can also be adapted for time-resolved studies, where time substitutes the y -axis, i.e., the stage remains immobile, and the detector records data for one row location (y) over time. In this setup, the user assigns the time-lapse parameters (number of time-lapse acquisitions, N_t ,

Table 2 Examples of optical and hyperspectral parameters to be set by the user prior to data acquisition

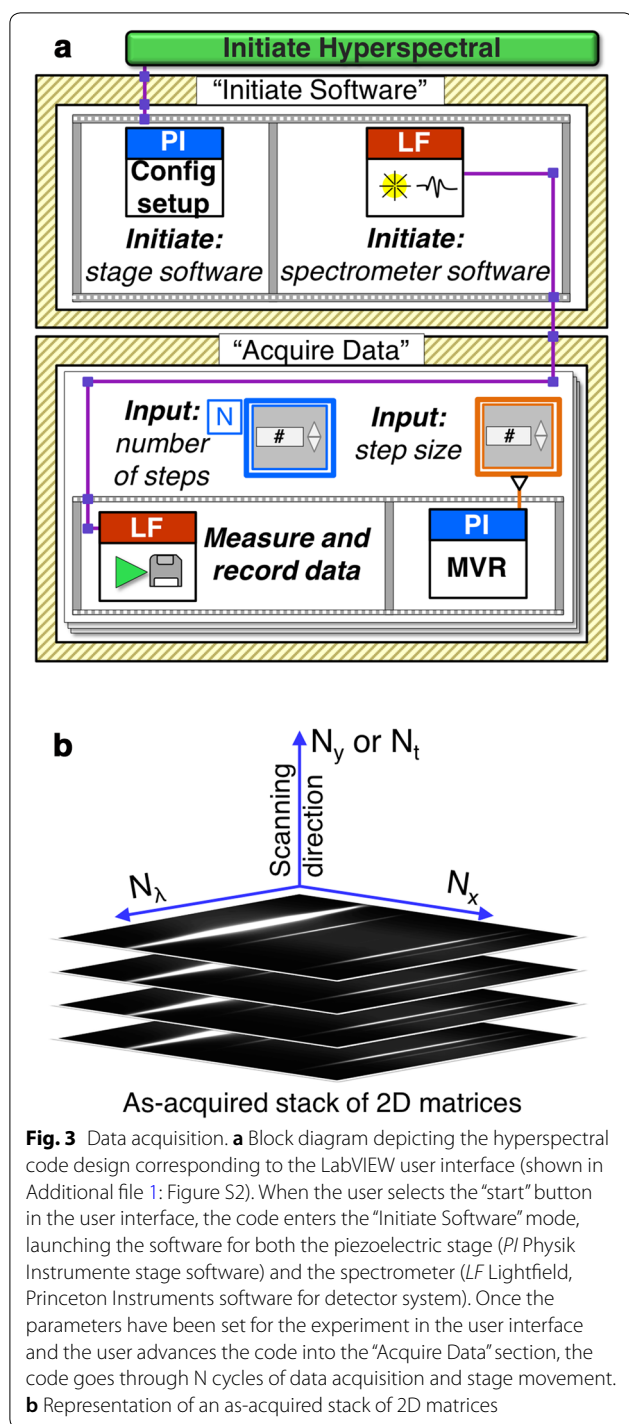
Optical parameters		Hyperspectral parameters	
Parameter	Example	Parameter	Example
Exposure time	0.5 s	Image width passed through slit	3.85 μm^a
Exposures/frame	4		1.54 μm^a
Grating grooves/mm	50	Step size	0.8 μm
Center wavelength	600 nm	Number of steps (N_y) ^b	250
		Number of time-lapse acquisitions (N_t) ^b	100
		Acquisition frequency	10 s

^a Objective magnification: 40 \times and 100 \times respectively

^b Only N_y or N_t is relevant in a given experiment

Table 3 Examples of experiment-specific computations utilized in data post-processing

Technique	Variable of interest	Computation	Example application
Transmission	Absorption	$-\log\left(\frac{\text{Sample transmittance}}{\text{Direct transmittance}}\right)$	2D materials electronic properties
Reflectance	Differential reflectance	$\frac{ \text{Sample reflectance} - \text{Substrate reflectance} }{\text{Substrate reflectance}}$	2D materials substrate interactions
Darkfield	Scattering	$\frac{\text{Particle scattering} - \text{Background scattering}}{\text{Lamp scattering} - \text{Dark scattering}}$	Plasmonic NPs single-particle studies



and acquisition frequency), and a series of 2D matrices (N_x, N_λ) are recorded, leading to an x - λ - t -datacube (N_x, N_λ, N_t).

Data post-processing

In the post-processing step (Fig. 4), the previously exported 2D matrices are imported into the Matlab-based

analysis software (code structure in Additional file 1: Figure S3, code details available upon request). The datacube contains up to $1024 \times 1024 \times N_y$ elements for spatial-scanning experiments and $1024 \times 1024 \times N_t$ elements for time-lapse experiments. The datacube is first integrated along the λ dimension to create an integrated spectrum, resulting in a picture-like 2D x - y matrix (Fig. 4c). The pixel locations for each ROI are then determined using the integrated spectrum image. These pixel values are then used to extract the λ element values (point spectra) within the datacube corresponding to the selected ROI. An ROI usually covers several pixels, such that several point spectra in a square array around the center of the ROI are typically added together. Experiment-specific computations (Table 3) are then conducted on the extracted data. The processed data are displayed (Fig. 4d) and written to CSV and Matlab workspace files.

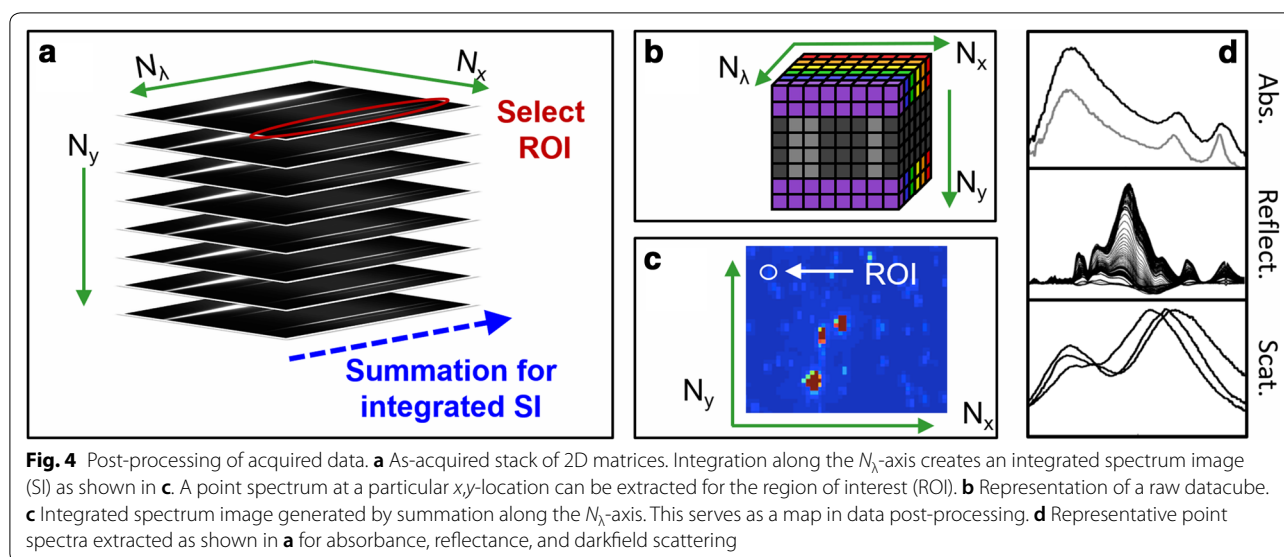
Results and discussion

Three case studies are described below. For each, a brief background is followed by key findings to exemplify the scope of applicability of MExS.

Case study 1. Transmission characterization of 2D transition metal dichalcogenides

TMDs have recently gained much attention because of their potential applications in electronics [8–11] and optoelectronics [8, 12–14]. At monolayer thickness, TMDs can exhibit direct electronic and optical bandgaps ranging from the visible to the near-infrared. Optical spectroscopy techniques such as photoluminescence (PL) and Raman are currently the key methods used in studying TMD properties such as bandgap energy, [15, 16] emission efficiency, [17–19] and defect density [19–21]. However, PL and Raman spectroscopies have limited quantum efficiency, making them unfit for high-throughput applications. The already-limited PL emission efficiency decreases sharply with increasing defect density. Moreover, both require rather specialized instrumentation [22, 23]. Because photons are absorbed regardless of the quenched PL emission, transmission MExS can overcome some of the yield limitations of PL, while providing simpler and faster operation than either PL or Raman.

MExS is a fast, large-scale approach to determine the optical bandgap energy and the extinction efficiency of TMDs. In this case study, MExS in transmission mode is used to identify and characterize monolayers of MoS_2 , MoSe_2 , WS_2 , and WSe_2 (Fig. 5). The samples were grown by chemical vapor deposition on quartz coverslips based on previously published techniques [24–27]. An example of optical image and wavelength-integrated hyperspectral datacube (forming a 2D image) is shown in Fig. 5a, b, and the rest are shown in Additional file 1: Figure S4.



The exciton peaks of the different TMD monolayers arise from direct bandgap transitions (A and B) at the K point of the Brillouin zone (Fig. 5c). Since the different TMDs have different bandgap energies, the position of the exciton peaks provides an accessible way to identify each material.

Case study 2. Reflectance characterization of 2D materials on nontransparent substrates

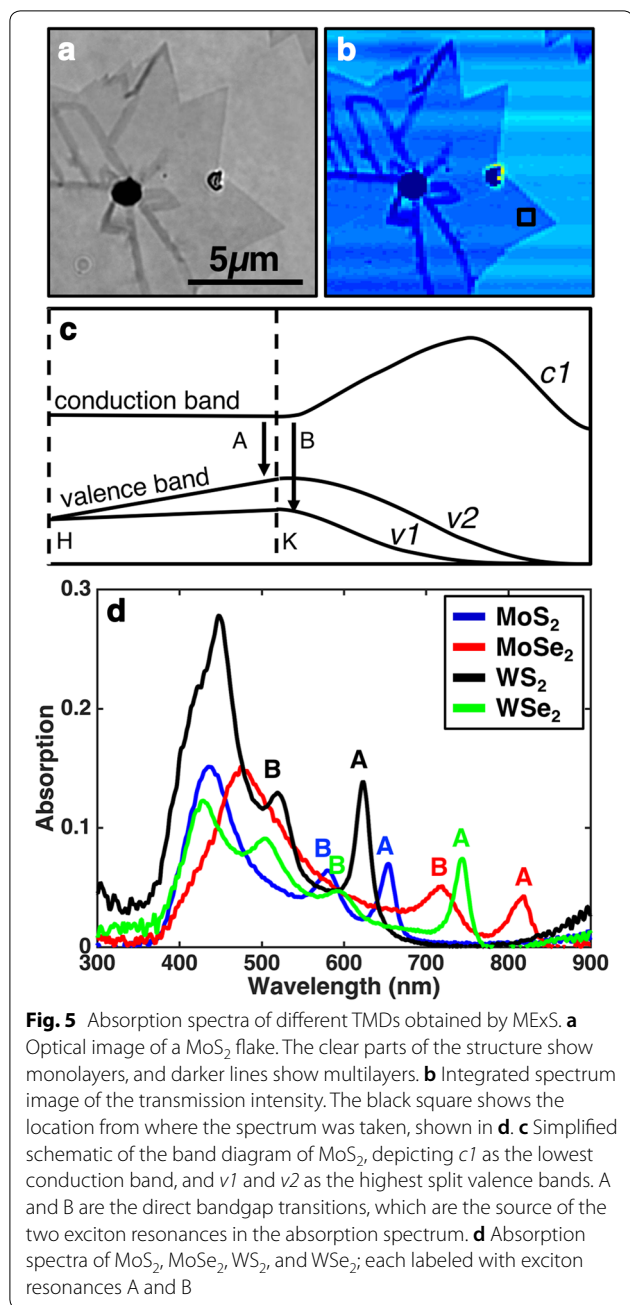
MExS in reflectance mode provides additional characterization functionality, opening the door to the study of nontransparent materials inaccessible with transmittance. Typical growth substrates for TMDs and other 2D materials (e.g., Cu and Si wafer) are opaque, as are many electrode materials (TiN, C) and surfaces of interest for antiwear/anticorrosion coatings (steel and other metal alloys). In this case study, the interaction between WS₂ and a TiN substrate was observed as an example of TMD behavior in corrosive environments, demonstrating the applicability of MExS to nontransparent substrates.

The samples used in this case study were prepared by using a micromechanical exfoliation technique that is described elsewhere [28]. The stacked layers of WS₂ are held together via van der Waals interactions, whereas the base layer is held to the TiN substrate via strong covalent bonds [28–31]. Various conditions were applied to these WS₂/TiN samples in order to simulate corrosive environments. Because the bandgap of the bulk state and monolayer state of WS₂ vary significantly (1.3 eV vs. 2.1 eV, respectively), the exciton energy can be used to track the layer thickness, providing insight into the effects of corrosive environments [8].

The integrated spectrum images (Fig. 6a, b) are referenced against the corresponding optical images (Fig. 6c, d) to locate the region of interest (identified here by an arrow). The reflectance signal contains a feature related to an exciton at 646 nm for the multilayer thin film (Fig. 6e). This exciton blue shifts to 616 nm as the film reaches monolayer thickness as a result of corrosion. The use of reflectance-mode MExS offers an opportunity to study large TMD flakes and monitor corresponding substrate interactions efficiently with the flexibility afforded by the use of nontransparent substrates.

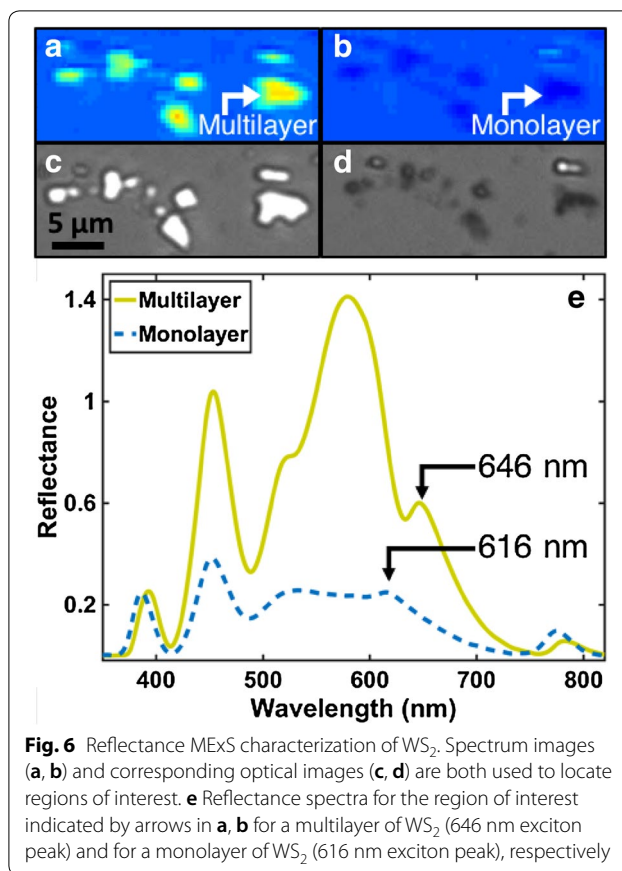
Case study 3. Darkfield scattering refractive index sensitivity of single gold nanoparticles: a sensitivity–structure correlation

MExS in scattering mode provides information about light–matter interactions in small scattering NPs. When light interacts with certain free-electron metal NPs (Au, Ag, Al, etc.), its electric field creates a collective electron oscillation called a localized surface plasmon resonance (LSPR) [32]. This resonance imparts bright colors and enhanced light–matter interaction properties to the NPs [33] and is dependent on NP size, shape, composition, and surrounding environment [34–36]. The latter can be used to construct plasmon sensors, as variations in the dielectric environment around the NP lead to approximately linear changes in LSPR frequency [33]. A measure of the sensing ability of a plasmonic system is the slope of the LSPR as a function of refractive index, i.e., the refractive index sensitivity (RIS) typically reported in nm per refractive index unit (nm/RIU) or eV/RIU. Values have been reported for Au nanorods, stars, crescents,



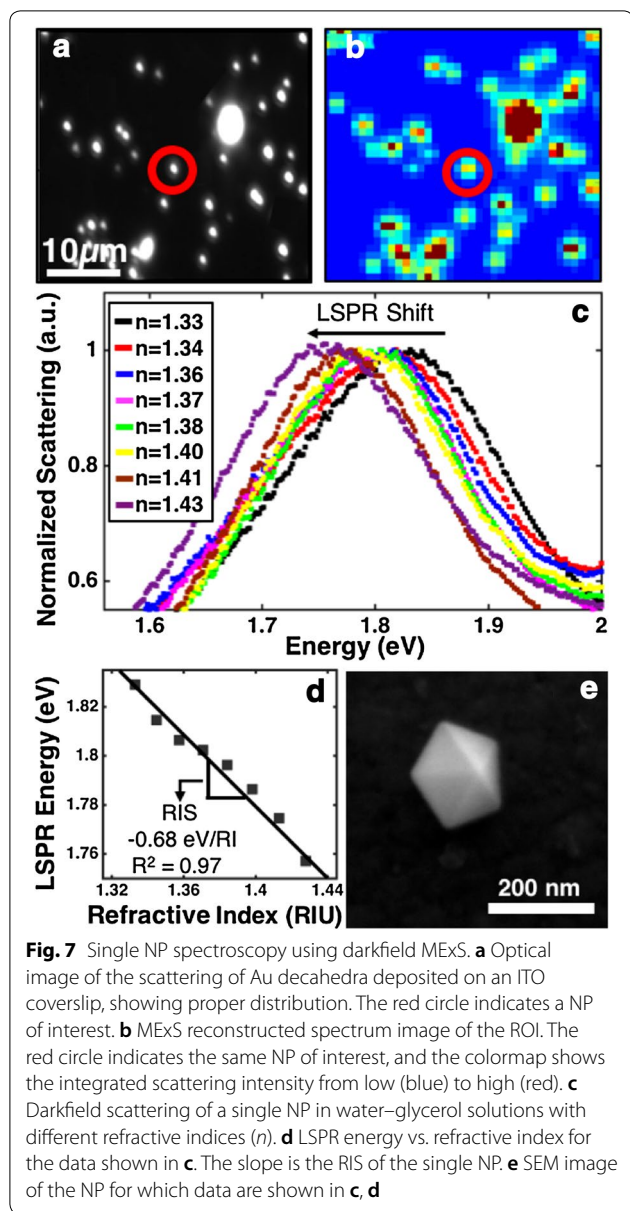
decahedra, bipyramids, and other shapes, and, together with the NP's LSPR energy and stability, are critical design rules for plasmon sensors [37–41]. An even more powerful expression is the sensing figure of merit (FOM), [42] defined as the RIS divided by the LSPR full width at half maximum (FWHM) in eV, i.e.,

$$\text{FOM} = \frac{\text{RIS}}{\text{FWHM}} \quad (1)$$



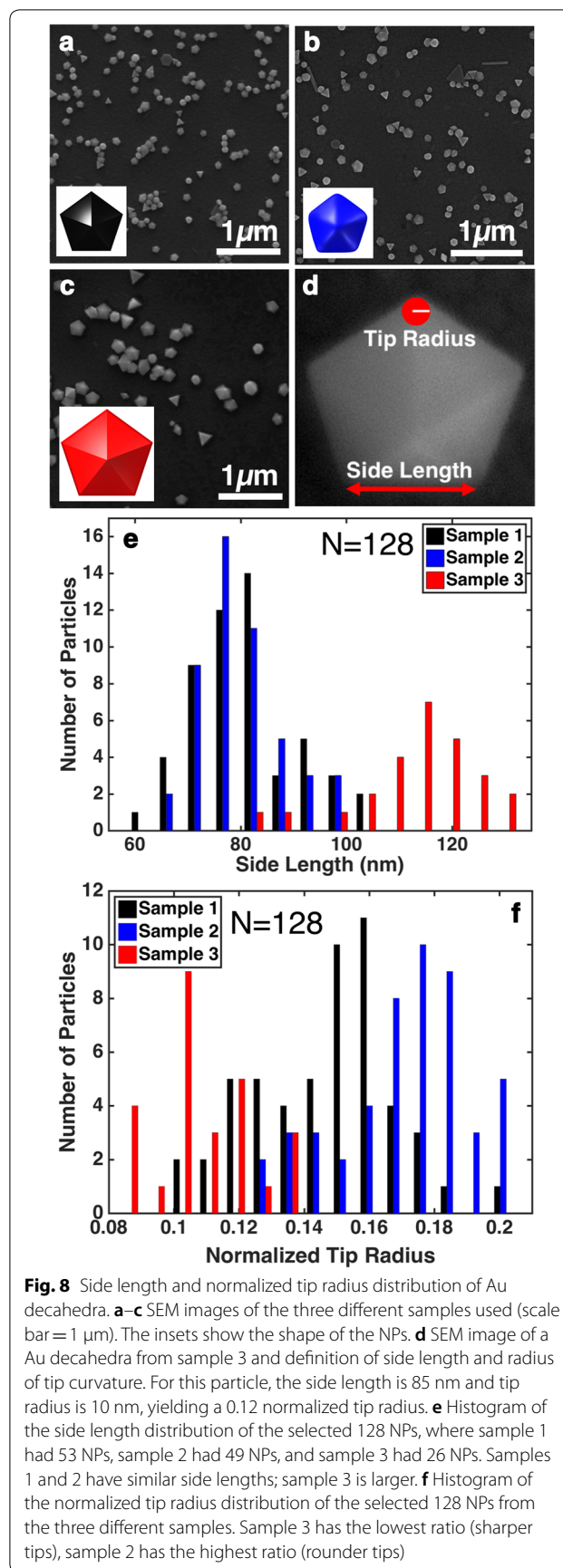
The FOM can be challenging to obtain because of heterogeneous broadening, requiring single NP measurements. In this case study, we show that MExS in scattering mode can easily provide the large statistics needed to extract RIS and FOM values at the single NP level, enabling detailed studies that are not blurred by the ensemble-averaging of bulk measurements.

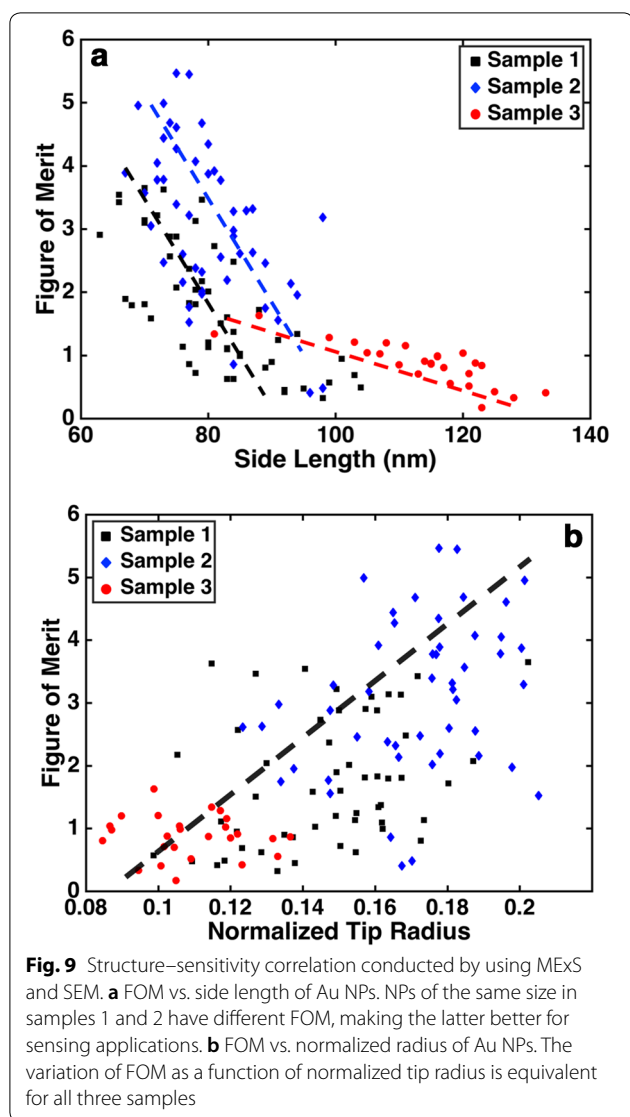
Three different batches of Au decahedra were synthesized using a previously published one-pot polyol process that allows both size and shape controls [43]. NPs were drop-cast on transparent and conductive indium tin oxide (ITO)-coated coverslips. The coverslips were marked with a scratch pattern for location reference. Coverslips were secured on a custom-built liquid cell and mounted on the microscope stage. The imaging camera was used to collect an optical map of the region of interest (Fig. 7a). Then, a MExS datacube was obtained for NPs submerged in solutions of varying refractive indices (water and glycerol; up to 70% glycerol), providing the single-particle darkfield scattering information needed to determine single-particle RIS. Representative data show the LSPR shift (Fig. 7c) as a function of RI, as well as the RIS (Fig. 7d) calculated from the slope of the linear relationship between the



LSPR peak energy of the NP vs. the refractive index of the medium [33].

Each ROI from the hyperspectral datacube can further be investigated with scanning electron microscopy (SEM, Fig. 7e), revealing structure–property relationships; here, the size and shape effect on RIS and FOM is observed. A total of 128 NPs were studied in this fashion (Figs. 7, 8, 9). The size and shape of each NP was measured from its SEM image with ImageJ, an open-source image analysis software. Before correlating the structure and sensitivity of the NPs, we aimed to better understand the features of each of the three NP batches using the side length and tip radius as indicators; note that we report, for easier





comparison, the normalized tip radius, i.e., tip radius divided by side length [44]. As shown in Fig. 8, the three samples offer significant structure variety: NPs in samples 1 and 2 have similar side length but different tip radius, while NPs in sample 3 have larger side length and relatively small normalized radius (i.e., sharper tips). Specifically, the average (standard deviation) side length was 81 (10), 80 (8), and 114 (12) for samples 1, 2, and 3, respectively; the average (standard deviation) normalized radius was 0.15 (0.02), 0.17 (0.02) and 0.109 (0.014) for samples 1, 2, and 3, respectively. From these structural variations emerge differences in LSPR properties. The LSPR energy, as expected, scales inversely with side length, i.e., LSPR energy is lower for bigger NPs (Additional file 1: Figure S5a) [1]. Interestingly, NPs in samples 1 and 2 have similar side lengths yet different LSPR energies because of the blue-shifting effect of corner rounding [44]. Lastly, NPs

in samples 1, 2, and 3 show a common trend as a function of tip radius, with rounder NPs having a higher LSPR energy (Additional file 1: Figure S5b).

Correlation of the structural parameters, at the single NP level, and the ability to obtain FWHM that are not heterogeneously broadened provides insight on structure-property relationships. MEXS/SEM analysis reveals that both RIS and FOM are greatest for small NPs (Additional file 1: Figure S6a and Fig. 9a, respectively). Samples 1 and 2 show large variance in RIS and FOM for NPs of comparable size, which can be attributed to corner rounding effects. A trend is again found by using normalized tip radius as the structural parameter, where rounder NPs are more sensitive and have higher FOM (Additional file 1: Figure S6b and Fig. 9b). These results indicate that side length is not the only structural parameter to be considered when identifying NPs suitable for sensing applications; the normalized tip radius appears to be a unifying structural parameter. Such study, requiring statistical information on many single NPs and multiple measurements (in different solutions) for each NP has uniquely been enabled by the high-throughput capabilities of MEXS and provides useful guidelines for NP selection in the design of label-free (bio)sensors.

Conclusions

We described a hyperspectral tool suitable for nanomaterials' characterization. The automation of the system's hardware and software relies on LabVIEW, and a Matlab-based analysis interface was developed for the data post-processing. We presented three different case studies that use the different optical modes in MEXS. First, by applying the transmission mode, different TMDs were identified quickly and without the need for lasers, taking advantage of the line-scanning operation of MEXS. Next, by applying the reflectance mode, the interaction between WS₂ flakes and a TiN substrate was studied. Finally, the optical sensitivity of Au NPs was determined by studying their scattering under different liquid media. We are convinced that MEXS is not only effective in the described examples, but can also be used in chemical/biological in situ experiments, thin film and coating analysis, or in situ catalytic mechanism studies.

Additional file

[Additional file 1.](#) Additional figures.

Author's contributions

AK developed the data acquisition and data analysis software, and performed the reflectance case study. EV designed optical setups and performed the transmission and darkfield case studies. ER designed the research. All authors

contributed equally to the writing of the paper. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

Data and material available upon request.

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