2016
doi:10.1017/S1431927622007838
Microsc. Microanal. 28 (Suppl 1), 2022

Probing Optical Phenomena of Si@MoS_2 Core-Shell Architectures at Nanoscale by Valence EELS

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In a core@shell structure, the nanoscale core can act as a cavity while the encapsulating two-dimensional material shell acts as a quantum emitter. The core is explained by Mie theory due to its size comparable to the wavelength of light. In Si@MoS_2, the dielectric silicon core hosts multiple optical Mie resonances and produces near-field enhancements of electric and magnetic fields [1]. Light can interact with the cavity's magnetic dipole resonance [2] and lead to improved light-matter interaction of the exciton transition dipole moment of MoS_2. This is a surface interaction effect, realizing the large exciton binding energy of MoS_2 even at room temperature [3]. Thus, optical-to-electrical conversions such as lasers and quantum information processing that had been otherwise limited due to the layered nature of MoS_2 can be achieved [2],[4].

Challenges associated with synthesizing a core-shell structure as shown in **Figure 1a** have traditionally hindered with its experimental investigation. Here, we use polycrystalline silicon nanospheres of 100-200 nm in diameter conformally encapsulated by MoS_2 layers (5-15 layers) in a chemical vapor deposition growth. Using transmission electron microscopy (TEM) and single-particle scattering spectroscopy, we demonstrate energy coupling in such architecture as magnetic dipole mode peak splitting in the scattering spectrum (**Figure 1b**). Correlation between morphology and optical response is depicted by TEM. In a system with core diameter of 143 nm and shell thickness of 8 nm (**Figure 1c**), we observe a coupling constant of 39 meV, approximately 1.5 times the that of reported nanoparticle-on-TMD film geometries [2].

To locally probe Si@MoS_2 optical properties in these complex architectures, we utilize electron energy loss spectroscopy (EELS). In special, the very low-loss region (0–50 eV) - valence EELS (VEELS) region - can be used to determine optical properties via Kramers–Kronig analysis (KKA). VEELS region contains information about excitations of outer shell electrons and thus the electronic structure of a specimen which determines its optical properties. The advantage of VEELS in combination with TEM is the high spatial resolution combined with acceptable energy resolution. We probe both the holistic Si@MoS_2 as well as its component features in a cross-sectioned Si@MoS_2, which are then compared to planar MoS_2 and silicon nanosphere standards.

The peaks in the imaginary part of the dielectric function (ε_2) reveal critical points in the electronic structure, and are present at ~2.8, 3.2, 3.7, 4.6, and 5.4 eV for the unencapsulated silicon nanosphere as shown in **Figure 2a** [5].

For the planar MoS_2, the ε_2 peaks appear at ~2.5, 3.2, 3.9, and 4.3 eV as shown in **Figure 2b** [6]. For the holistic Si@MoS_2 core-shell system, the dielectric function surprisingly shows one outstanding, narrow peak in ε_2 at ~3.8 eV as shown in **Figure 2c**. This is likely from a dominant critical point in the hybridized electronic structure. A localized study is required to trace the transforming dielectric function upon integrating the MoS_2 and silicon nanosphere into a core-shell structure. Examining the cross-sectioned sample point-by-point (**Figure 2d**), we observe that the dielectric function at the core of the cross-sectioned core-shell, which lacks the shell component, resembles the that of the unencapsulated core (**Figure 2e**). Approaching the shell, ε_2 gradually narrows and begins to resemble that of planar MoS_2 although there is a red-shift possibly due to band structure changes from geometric curvature (**Figure 2f**). The dielectric function here also begins to resemble that of the holistic Si@MoS_2 as signals from both silicon and MoS_2 are collected.

By demonstrating resonance coupling at the scale of individual Si@MoS_2 core-shell structure, we propel transition metal dichalcogenide applications in nanophotonic and optoelectronic devices. We further explore localized Si@MoS_2 dielectric functions using EELS and KKA. As the dielectric function encodes information on various optical properties such as reflectivity and transmittivity, we propose EELS as a powerful technique to understand the evolution of optical properties in complex heterostructures at the nanoscale [7].

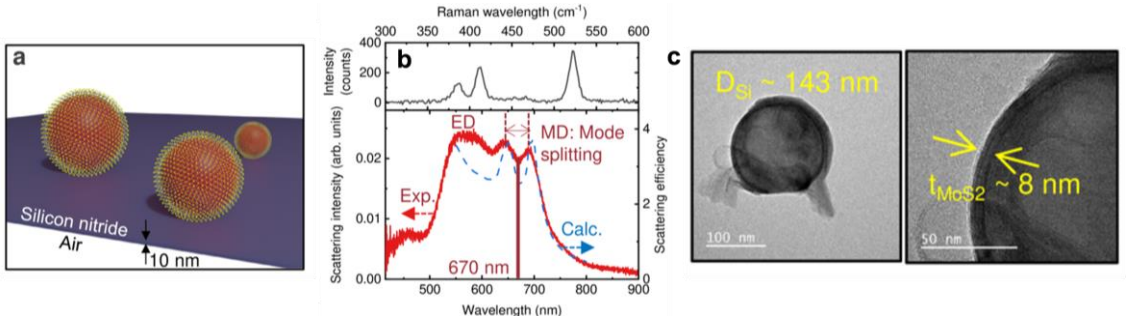

Figure 1. a) Schematic of Si@MoS_2 on silicon nitride substrate. b) Raman spectrum of Si@MoS_2 on Si/SiO_2 substrate [top]. Experimental magnetic dipole mode splitting at 670 nm, in agreement with calculations [bottom]. c) TEM images of Si@MoS_2 system from which (b) is measured.

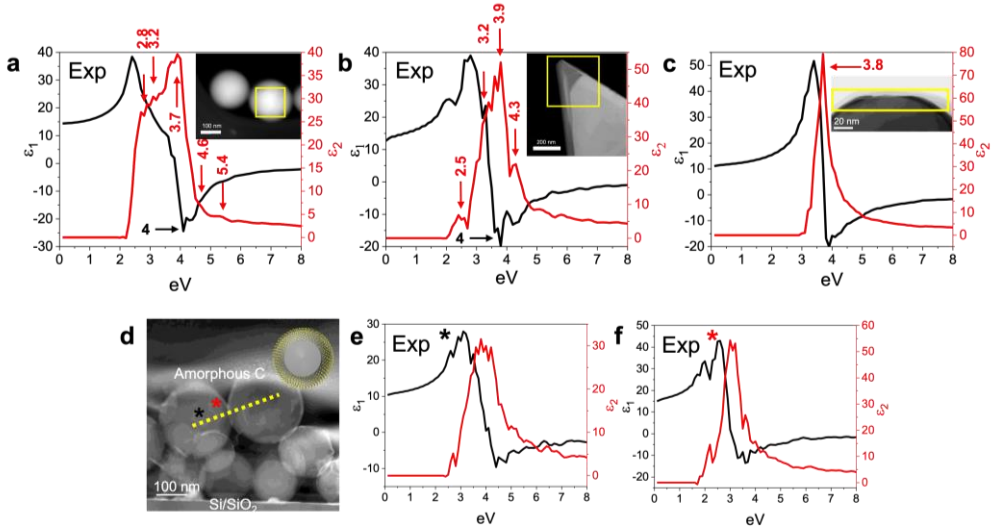

Figure 2. Experimental dielectric functions of a) silicon nanosphere, b) planar MoS_2, and c) Si@MoS_2. Inset: region from which the functions are acquired. d) Scanning TEM image of cross-sectional Si@MoS_2 with line profile in yellow. Dielectric functions at e) the core, and f) near core-shell interface.

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[7] This material is based upon work primarily supported by the National Science Foundation (NSF) under Grant No. DMR-1929356. This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the SHyNE Resource (NSF-ECCS 2025633), the IIN, and Northwestern's MRSEC program (NSF DMR-1720139).