Probing Materials Functionality with Aberration-Corrected STEM and First-Principles Theory

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The successful correction of lens aberrations has greatly advanced the ability of the scanning transmission electron microscope (STEM) to provide direct, real space imaging at atomic resolution [1]. Data generated by aberration-corrected STEM is ideally suited for interpretation through density functional theory (DFT), a strategy that can provide the deepest insights into the origin of materials properties, especially in low-dimensional systems such as defects, interfaces, nanostructures and point defects.

Interfaces in complex oxide heterostructures show many surprising properties. Aberration corrected STEM images can provide (projected) atomic coordinates with precision of a few pm. Examples will be shown of $BiFeO_3$, mapping polarization, lattice parameter and octahedral rotations across interfaces unit cell by unit cell [2], and the origin of colossal ionic conductivity in $SrTiO_3/Y_2O_3$-stabilized ZrO_2 superlattices [3-5].

Nanocrystals exhibit structures and properties with no relation to the bulk, for example the white-light emission from individual CdSe nanoclusters. Real space imaging combined with density functional calculations have unraveled the origin of such surprising properties. Figure 1 shows annular dark field (ADF) images of CdSe nanocrystals with diameters of 7 nm, 5 nm and 3 nm. The 7 nm nanocrystals emit red light, the 5 nm nanocrystals emit orange light and the 3 nm nanocrystals emit green light. These particles are composed of a wurtzite crystal core surrounded by a disordered surface layer of roughly a nanometer in thickness. Each subsequent STEM image shows a different configuration of this dynamic surface layer, while the crystal cores remain stable. On reducing the size to 2 nm there is no longer any crystalline core, and the entire structure changes continuously under the beam (Fig. 2). No change in the rate of the dynamic fluctuations was perceivable between accelerating voltages of 60, 100 and 300 kV as well as from beam currents varying up to a factor of five. Under illumination by ultraviolet light we might expect the nanoparticles to heat up and exhibit similar structural fluxionality as under the electron beam. DFT simulations reveal that the evolving electronic structure produces a range of possible emission energies that corresponds to the width of the emission spectrum observed experimentally.

Finally, the direct imaging and identification of point defect configurations in monolayer graphene will be presented. Such point defects create localized plasmon resonances of sub-nm extent as shown in Fig. 3. This observation suggests that the point defect complex acts as an atomic-scale antenna in the petaHertz (10^{15} Hz) frequency range (11 eV is equivalent to a frequency in the order of 10^{15} Hz), and is the smallest resonant structure seen to date [6].

References
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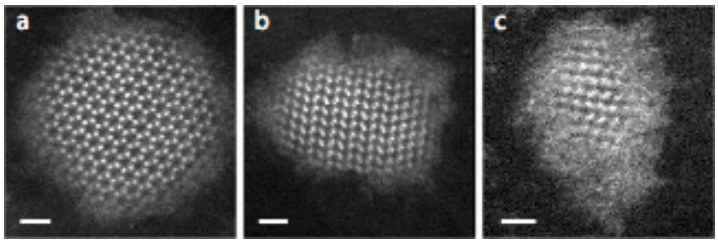

FIG. 1. High resolution Z-contrast images of CdSe nanocrystals with diameters of (a) 7 nm, (b) 5 nm and (c) 3 nm, which emit red, orange and green light respectively. Scale bars: 1 nm.

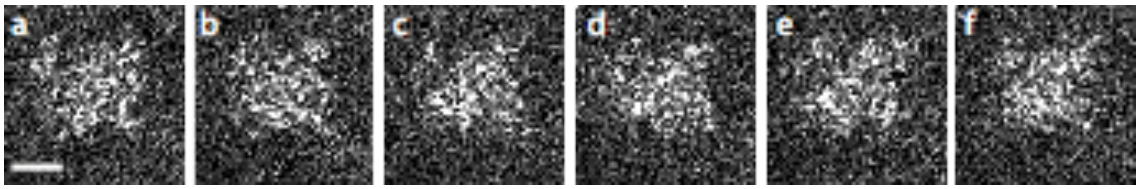

FIG. 2. (a-f) Frames from a high resolution ADF movie of an ultrasmall CdSe nanocluster showing the continuous atomic motions seen in all the samples that emit white light. Scale bar: 1 nm.

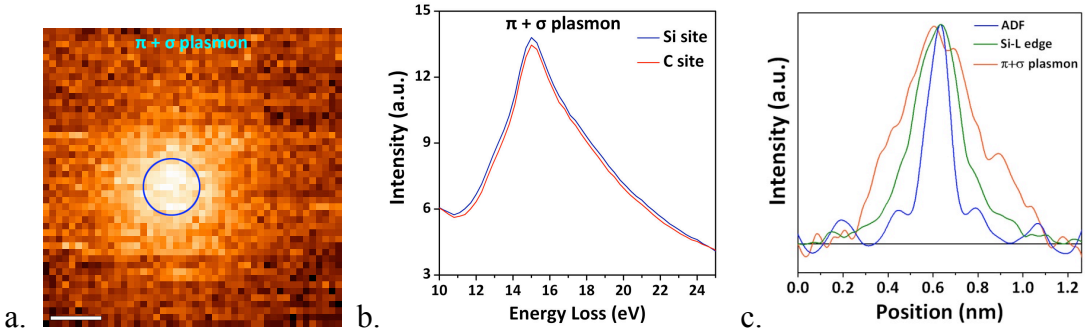

FIG 3. (a) Plasmon map (11-18 eV) showing localized enhancement of the π + σ plasmon at a substitutional Si atom. (b) Comparison of the graphene π + σ plasmon spectra, extracted from the Si atomic site and from the carbon site. (c) Comparison of the delocalization of the ADF signal, the Si-L edge signal, and the enhanced plasmon intensity from the Si atom. Scale bar: 0.2 nm. (a) reproduced from Ref [6].