Atomic Structure and Spectroscopy of Single Metal (Cr, V) Substitutional Dopants in Monolayer MoS_2

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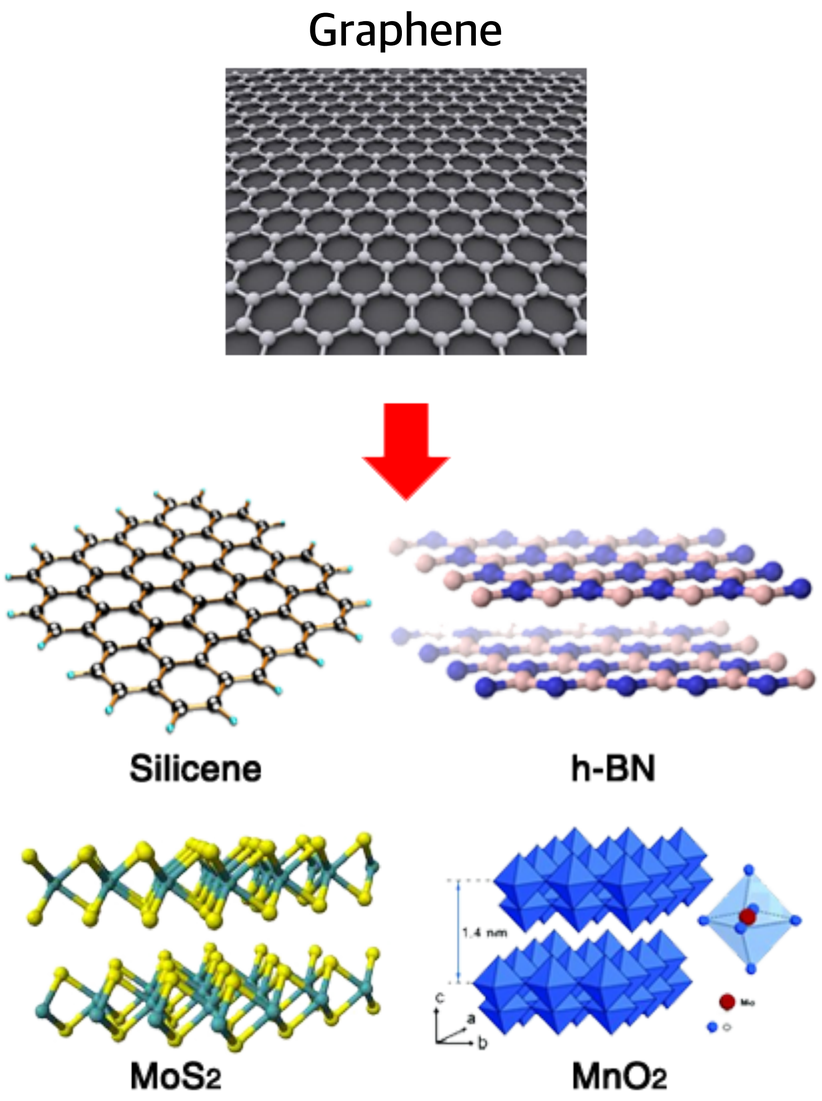
Various 2D materials and MoS_2



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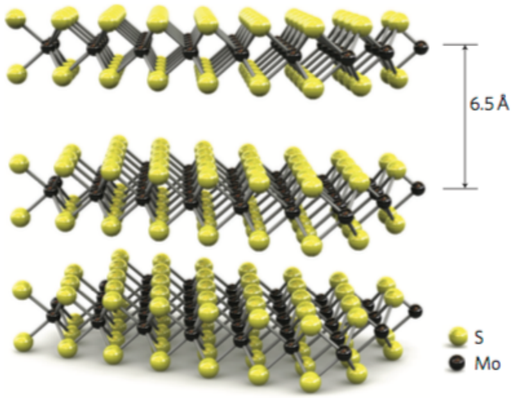

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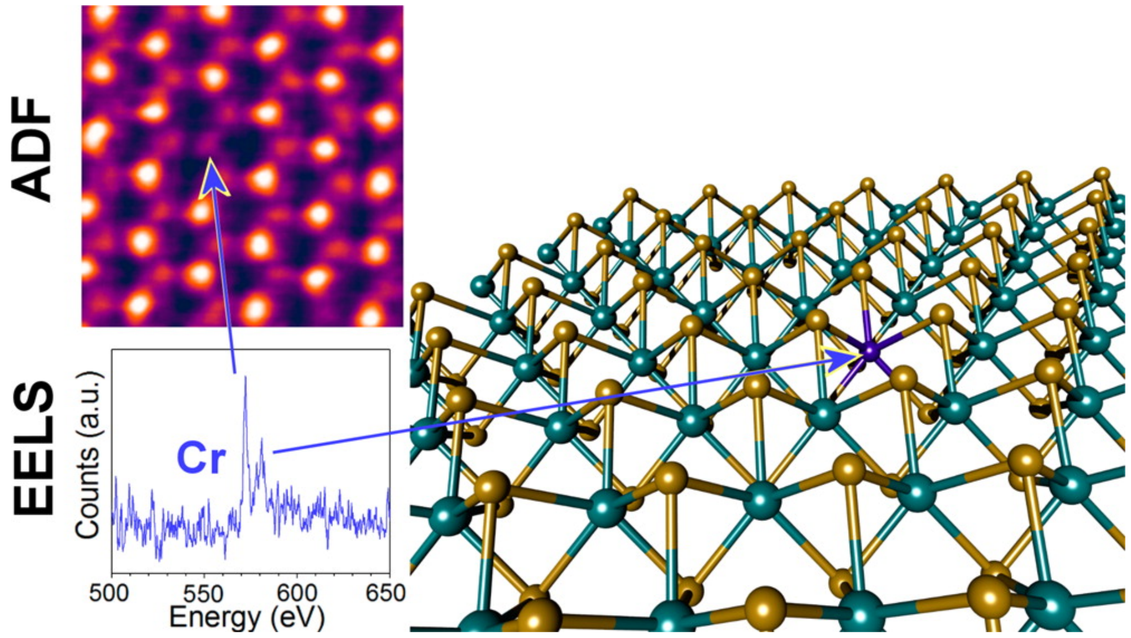
MoS_2 (TMD)

- Hexagonal layered structure
- Semiconductor:
  - Bulk: indirect, 1.29 eV
  - Monolayer: direct, 1.90 eV
- Large excitonic effect
- Applications: catalysis, transistor, optoelectronics

Our work: Cr and V dopants in MoS_2 monolayer



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- Substitutional Cr and V atom at Mo site were identified using annular dark field scanning transmission electron microscopy (ADF-STEM) and electron energy loss spectroscopy (EELS)
- Cr and V are stable under electron irradiation and high temperature
- DFT calculations for formation energy and density of states of charged dopants

Methods: MoS_2 synthesis and imaging

[by Prof. Jamie H. Warner (U. of Oxford) group]

- CVD grown monolayer MoS_2 using MoO_3 and sulfur
- MoS_2 is transferred by PMMA scaffold technique to holey Si_3N_4 TEM grid
- ADF-STEM, AC-TEM imaging and EELS were performed at an accelerating voltage of 60 kV and 80 kV
- In situ heating holder was used for high-temperature imaging

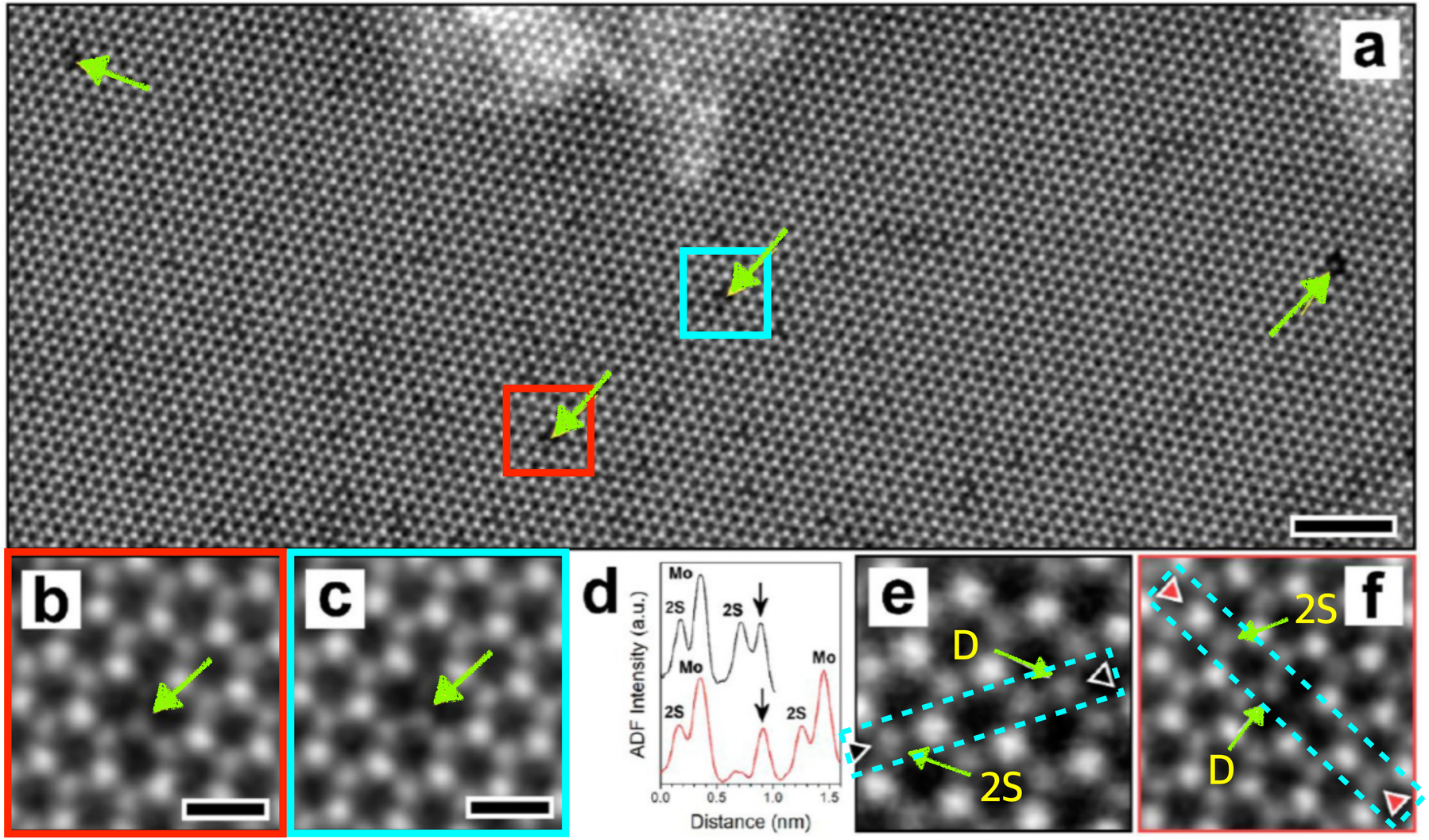
Methods: DFT calculations

$$E_{\text{form}}^{\text{iso}} = E_{\text{tot}}^{\text{defect}} - E_{\text{tot}}^{\text{pristine}} - \sum_i N_i \mu_i$$
$$+ q\left(\epsilon_{\text{VBM}}^{\text{pristine}} + E_{\text{Fermi}}\right) + E_{\text{corr}},$$

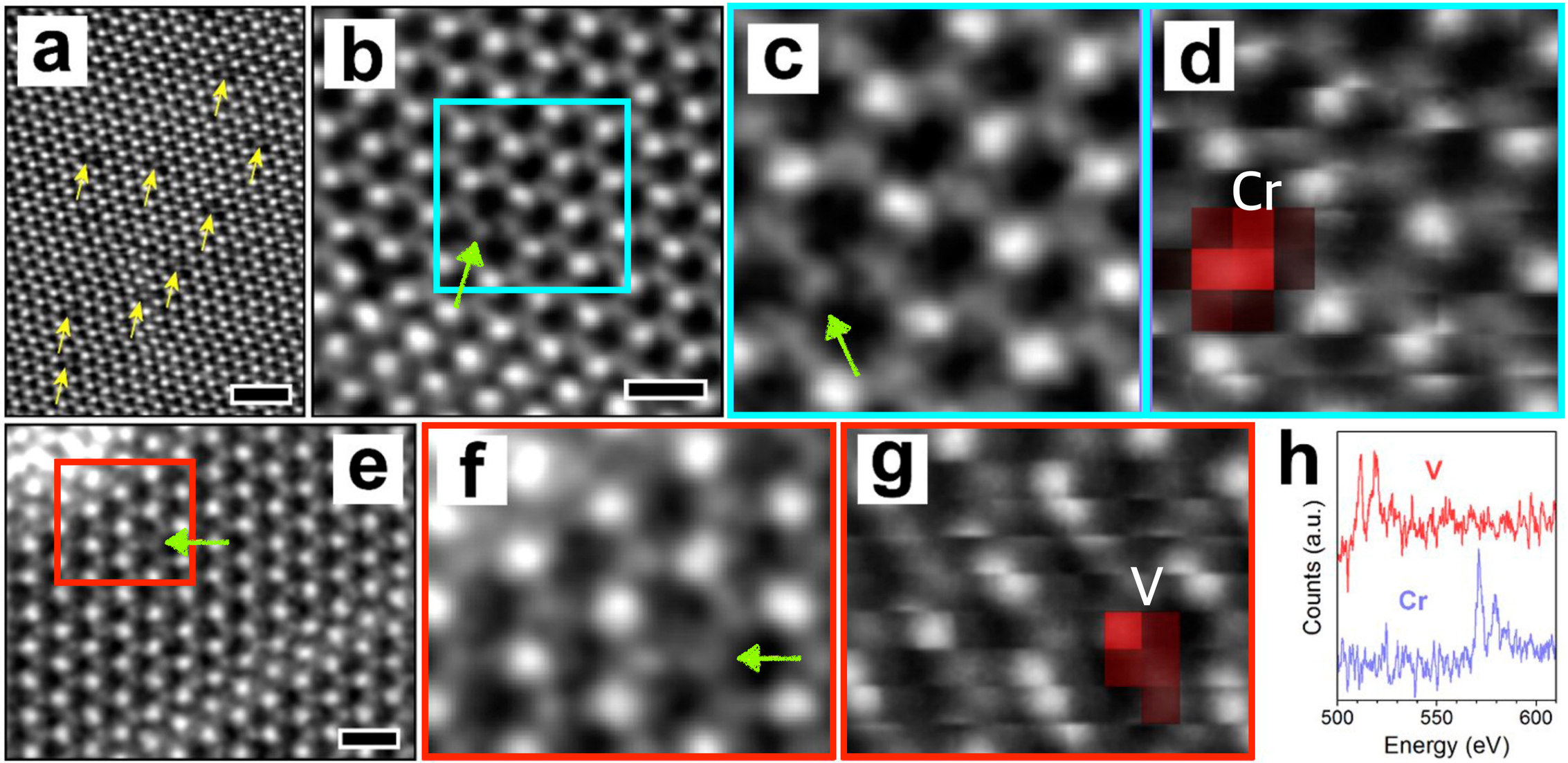
- DFT calculation using VASP code
- GGA with Perdew-Burke-Ernzerhof (PBE) functional was used for the exchange-correlation potential
- Formation energies of the charged defects were calculated using appropriate correction scheme
- All the experimentally known stable binary phases of Cr (or V) and S were calculated to determine chemical potentials of Cr and V

Results and discussion

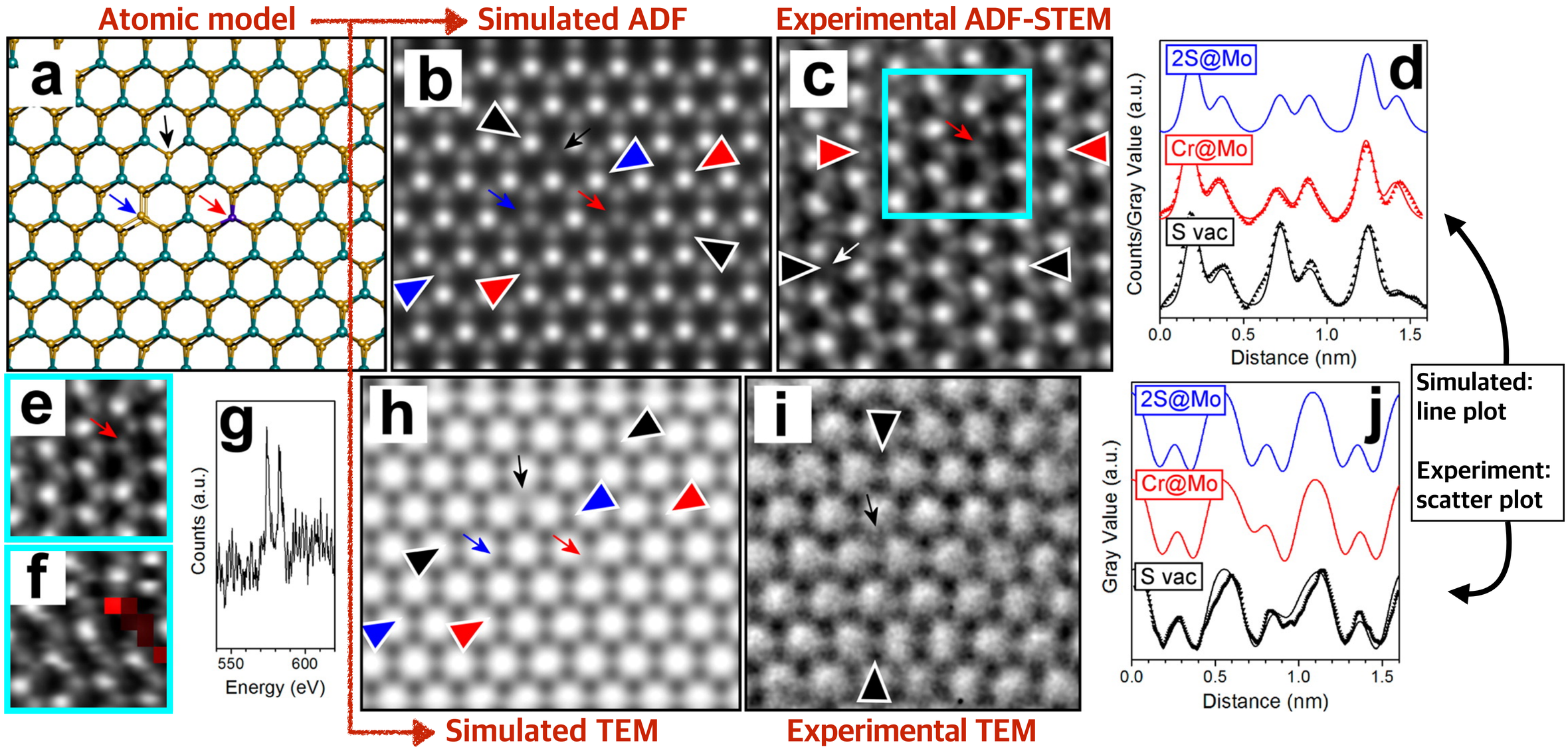
Low contrast intensities at Mo site



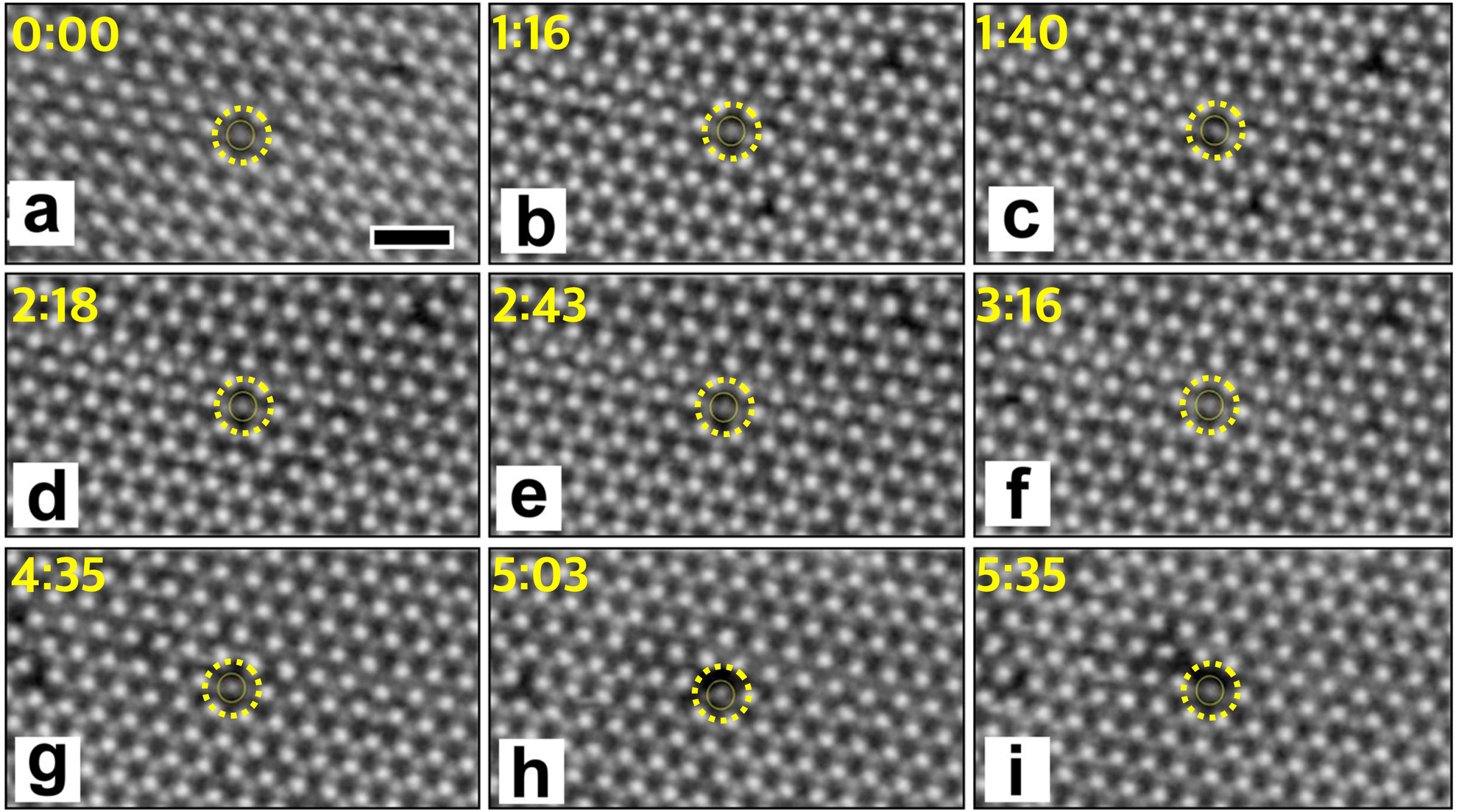
EELS mapping of single atom Cr and V substitution



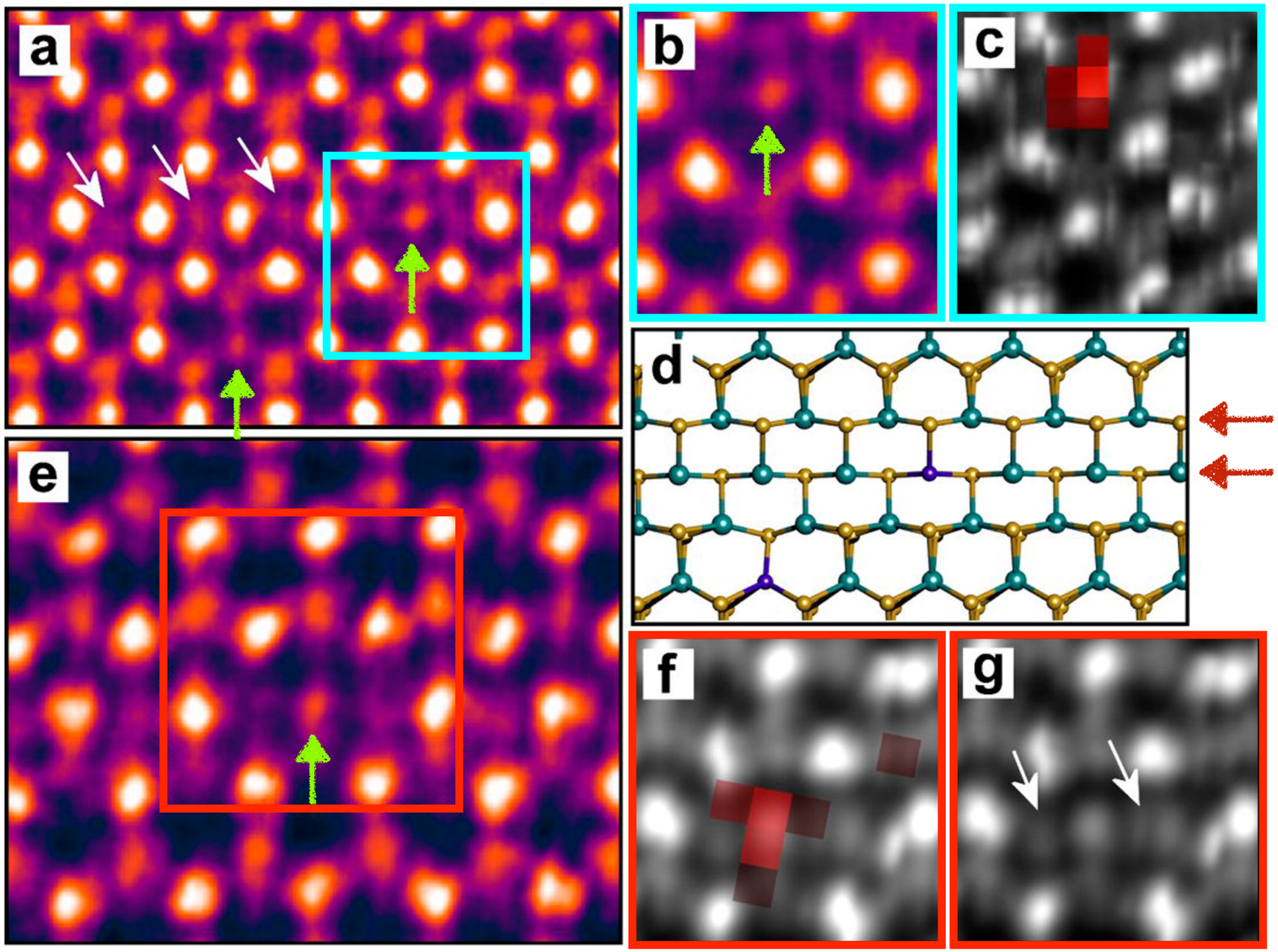
Distinguishing Cr and 2S by ADF-STEM image simulation



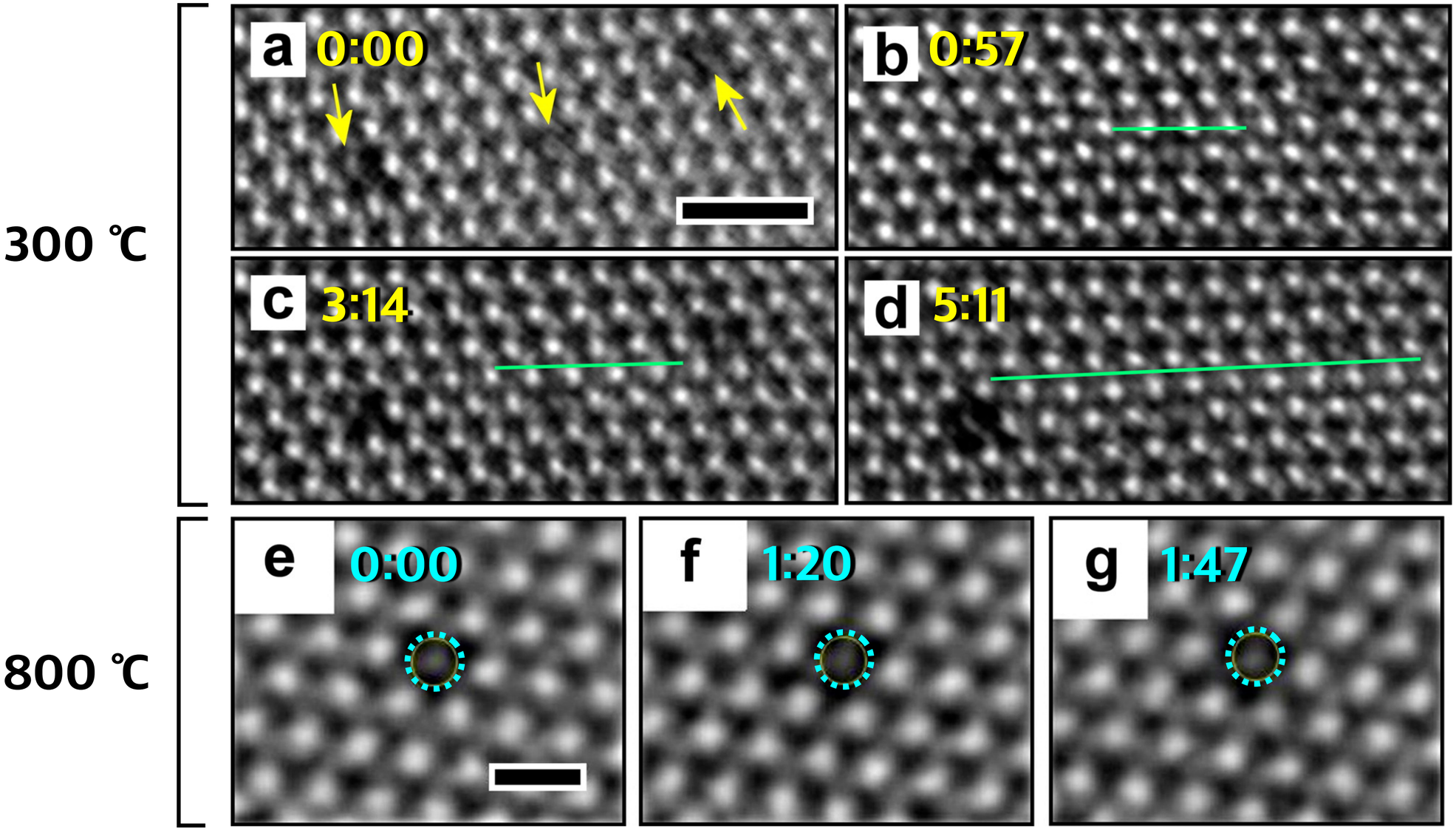
Room temperature stability of substitutional metal atom



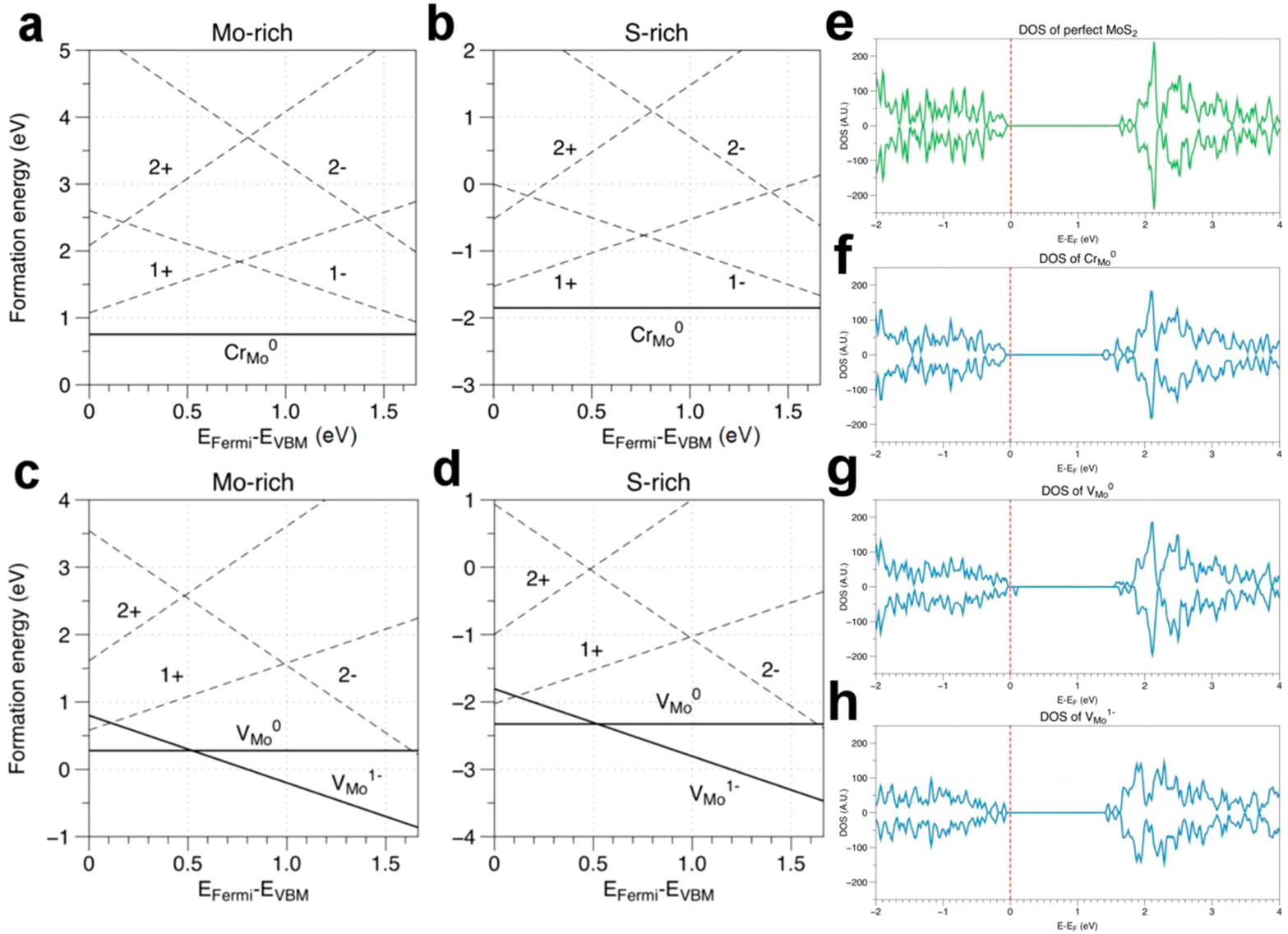
Inclusion of Cr dopant in S vacancy line defects at high temperature



High temperature stability of metal substitutional atoms



DFT calculated formation energies and DOS of Cr and V



Conclusion

- The presence of single atom substitutions of Cr and V for Mo in CVD monolayer MoS_2 has been experimentally demonstrated by a combination of ADF-STEM and EELS mapping
- Imaging of Cr with S vacancy line defects and time-series imaging at temperatures up to 800 ℃ confirm that the Cr substitution is a stable dopant configuration
- DFT calculations revealed formation energies, charge states, and change to the electronic properties by substitutional dopant

Thank you