# Bandgap Tuning in Monolayer MoSe2 Induced by Selenium Vacancies

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Transition metal dichalcogenide (TMD) monolayers hold great promise for advancing next-generation electronics and optoelectronics. The synthesis of large-area TMD monolayers with a high degree of crystallinity is crucial for enabling mass production and real-world applications. However, the influence of structural defects on the optical properties of these two-dimensional (2D) materials remains unclear. In this study, we demonstrate a method for synthesizing $MoSe_2$ monolayers with high concentrations of selenium vacancies. Using liquid-assisted chemical vapor deposition and by controlling the duration of the selenium feedstock during synthesis, we were able to introduce selenium vacancies into $MoSe_2$ monolayer flakes. As the flakes grew, we observed that double-selenium vacancies became more frequent at the edges of the flakes when compared to the central regions, whereas the concentration of single-selenium vacancies remained relatively constant throughout the entire flake of $MoSe_2$. These observations were confirmed by atomic-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Furthermore, femtosecond transient absorption spectroscopy revealed a notably accelerated decay rate at the edges of the flakes, implying a higher likelihood of nonradiative transitions related to defects (e.g.double-selenium vacancies). Interestingly, photoluminescence (PL) spectroscopy showed an increase of approximately 40 meVin the energy of emission for both excitons A and B at the flake's edges when compared to the central region. Laser power-dependent PL measurements performed at the edge of the samples indicated a linear power relationship with the emission on the edge, suggesting the nature of a free exciton. Through first-principles density functional theory calculations, we confirmed that the selenium vacancy concentration is correlated with an increased bulk bandgap, which confirmed our observations in the PL measurements. These findings not only unveil the growth mechanism of liquid-assisted chemical vapor deposition on $MoSe_2$, but also contribute to a better understanding of the role of double-selenium vacancies in tailoring the optical properties of $MoSe_2$ monolayers.”