# Supporting Information for

# Simultaneous Surface-Enhanced Resonant Raman and Fluorescence Spectroscopy of Monolayer $MoSe_2$: Determination of Ultrafast Decay Rates in Nanometer Dimension


**Yexin Zhang,** [†] **Wen Chen,** [†] **Tong Fu,** [†] **Jiawei Sun,** [‡] **Daxiao Zhang,** [†] **Yang Li,** [†] **Shunping Zhang,** [*, †] **Hongxing Xu,** [*, †, ‡]

[†]School of Physics and Technology, Center for Nanoscience and Nanotechnology, and Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education, Wuhan University, Wuhan 430072, China.

[‡]The Institute for Advanced Studies, Wuhan University, Wuhan 430072, China.

**Corresponding Author**

*E-mail: spzhang@whu.edu.cn. Phone: +8627 68752219.

*E-mail: hxxu@whu.edu.cn. Phone: +8627 68752253.

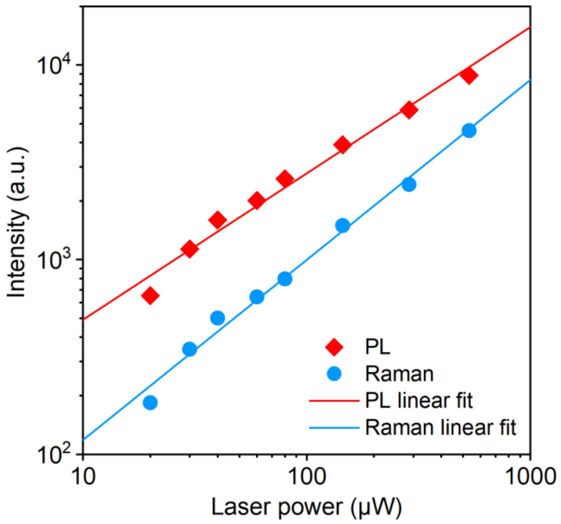


**Figure S1. SERS and SEF intensities of a $MoSe_2$-NCOM as a function of excitation power.** The SERS and SEF intensities were taken from the $E^1_{2g}$ peak and the shaded red region in Figure 2 (top panel), which both show a linear power dependence.

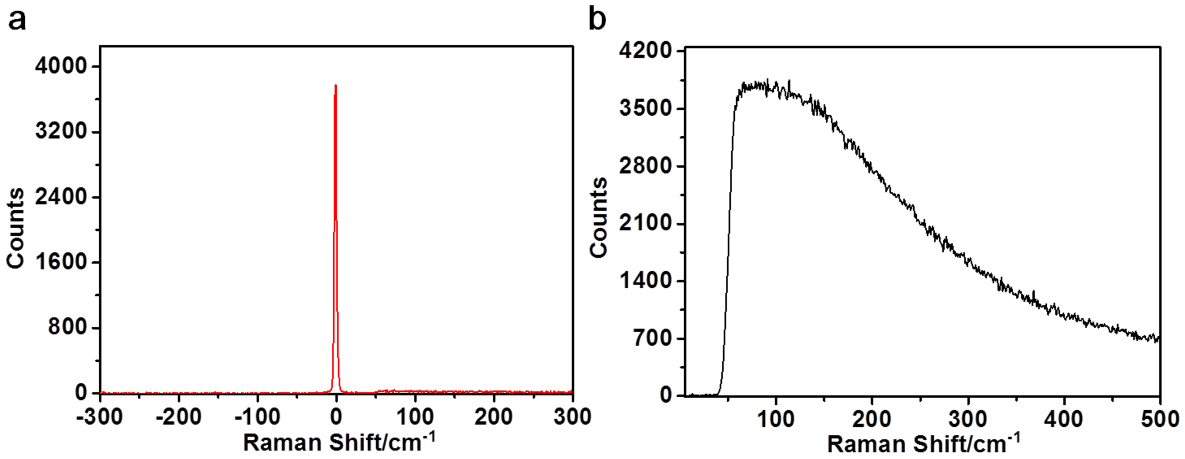


**Figure S2. Measurement of quantum yield of 1L $MoSe_2$ on quartz.** (**a**) Collection spectrum of 785 laser. (**b**) PL spectrum of 1L $MoSe_2$ on quartz.

The quantum yield of the 1L $MoSe_2$ on quartz was obtained by $Q^0 = I_{PL} / I_{exc} f_{abs}$ where $I_{exc}$ the excitation and $I_{PL}$ the PL emission photon counts, $f_{abs}$ is the absorption efficiency of 1L $MoSe_2$ at 785 nm, which is taken to ~7%. $I_{PL}$ can be readout by the spectrometer, and $I_{exc}$ was obtained by $I_{exc} = \eta P_{exc}$, where the $P_{exc}$ is of the 785 nm laser power for the PL excitation. $\eta$ is the collection efficiency of the spectrometer, which means the conversion efficiency from the laser power at the back aperture of the objective to the readout photon counts on the spectrometer. To obtain $\eta$, the 785 nm laser with given power $P_{ref}$ was illuminated on a mirror (Max mirror, Semrock) using the same configuration as in the PL measurements, while the reflected light was collected by the same collection setup to readout the photon counts $I_{ref}$, thus $\eta = I_{ref}/P_{ref}$. Then we can obtain the quantum yield $Q^0$, which is 3.6%.

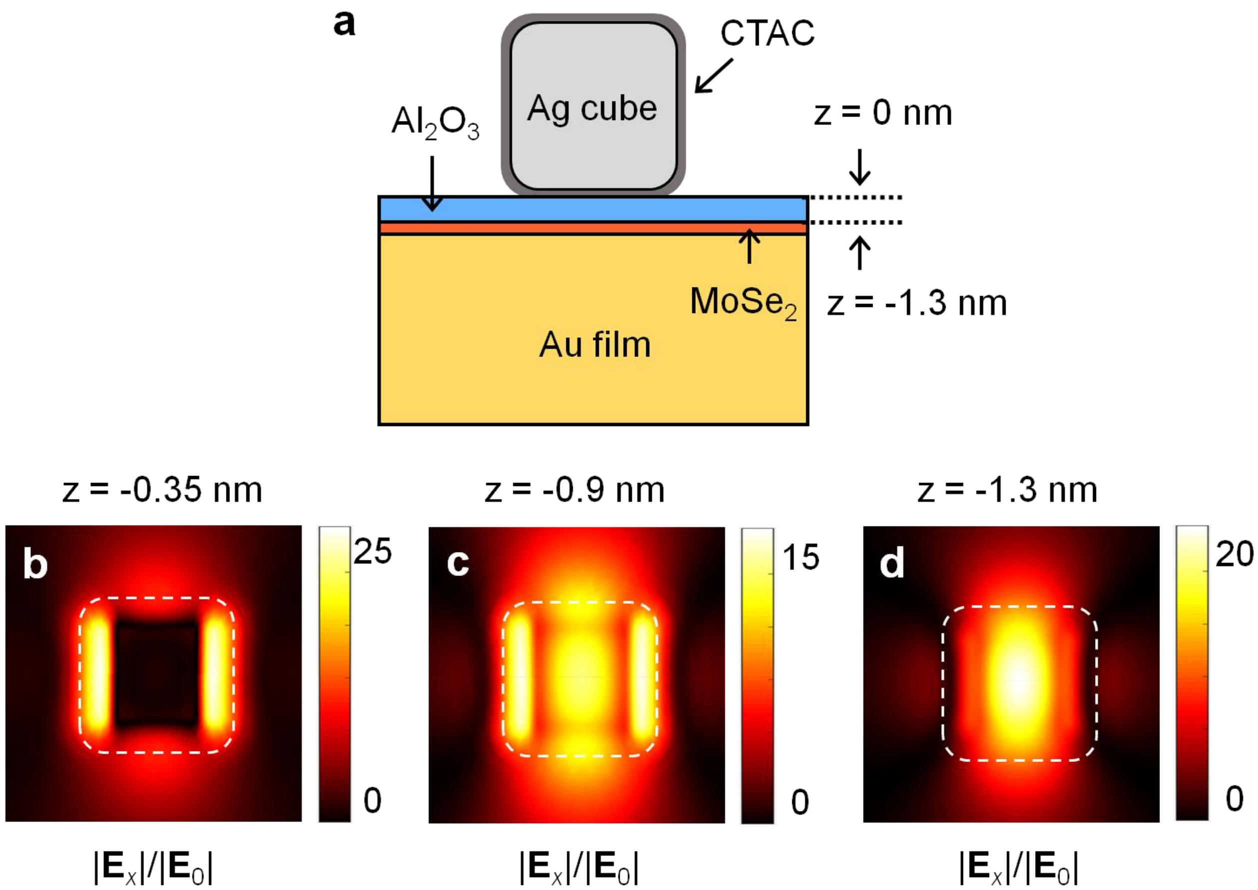


**Figure S3. In-plane local field distributions of the M mode at different gap position.** (**a**) Schematic of the $MoSe_2$-NCOM that defines the plane position in the gap region. (**b-d**) the electric field distributions of the $MoSe_2$-NCOM with 14-nm-thick $Al_2O_3$ coating at 785 nm in the x-direction, with in-plane cross-section located at z = -0.35 nm (**b**), -0.9 nm (**c**) and -1.3 nm (**d**).

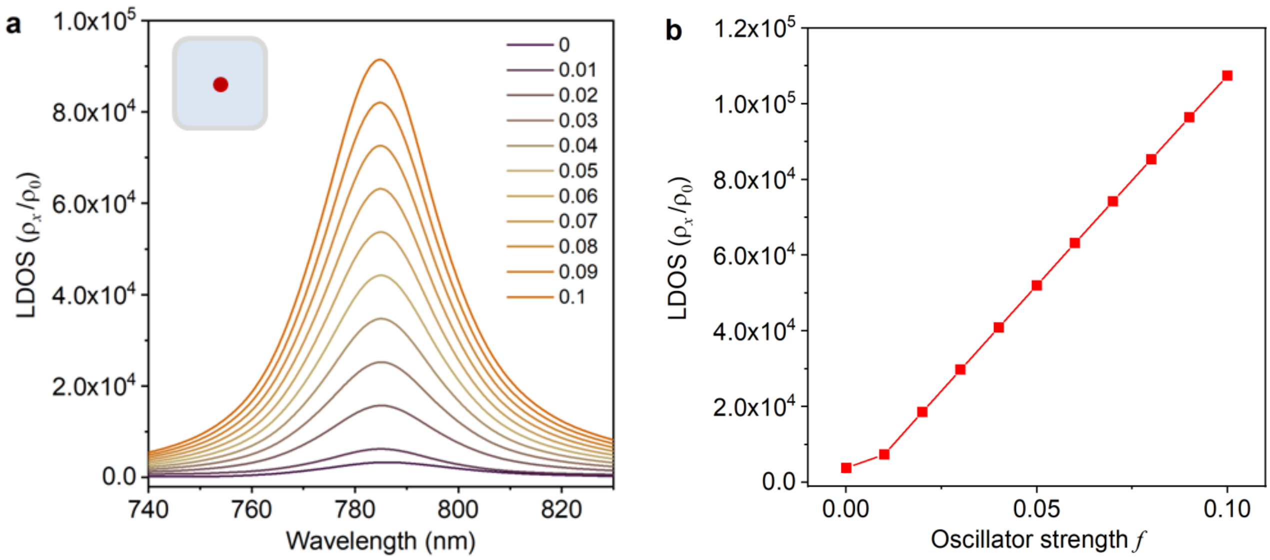


**Figure S4. In-plane LDOS of a NCOM nanocavity as a function of the oscillator strength *f* of the A-excitons.** (**a**) In-plane LDOS spectra of a NCOM nanocavity with a 14-nm-thick $Al_2O_3$ coating by setting the value of *f* from 0.01 to 0.1. The inset shows the top view of the Ag nanocube with a red dot representing the position of a dipole. (**b**) The maximum in-plane LDOS as a function of *f*, showing a linear increase of the LDOS as *f* increases.

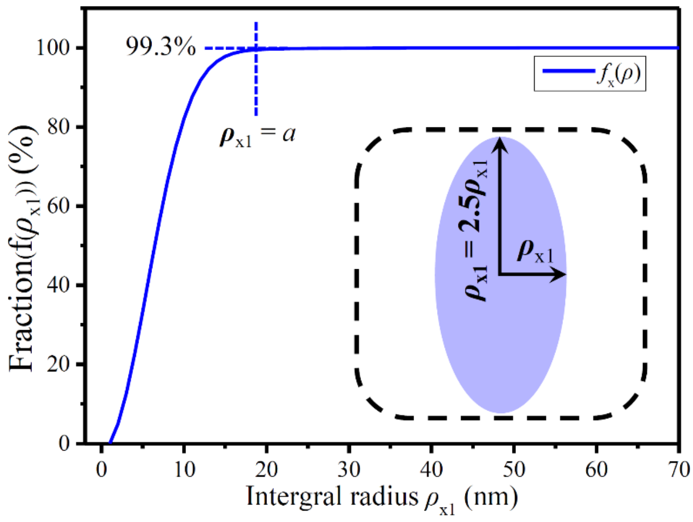


**Figure S5. Fraction $f_x$ as a function of integral minor axis $\rho_{x1}$. The inset shows the definition of integral radius $\rho_{x1}$, the integral region is an ellipse and the ratio between the major and minor axis is 2.5 ($\rho_{x2}$= 2.5$\rho_{x1}$). The effective local field area $\pi ab$ is determined by increasing $\rho_{x1} = a$ and $\rho_{x2} = b$ until the fraction reaches $f_x = 1 - e^{-5}$ (~99.3%).**

From Figure S3d, the local field of $E_x$ is mainly below the cube and distributed as an ellipse shape. As a result, the effective "hotspot" area is determined as an ellipse with minor axis $a$ and major axis $b$. The effective "hotspot" area is calculated by defining a fraction $f_x$ as the ratio of the $x$ component of SERS EF contributed from an ellipse area $\pi\rho_{x1}\rho_{x2}$ centered at the nanogap region to that from the collection area (considered as infinity):

$$f_x(\rho_x) = \int_0^{\pi\rho_{x1}\rho_{x2}} |E_x|^4/|E_{0x}|^4 ds / \int_0^{\infty} |E_x|^4/|E_{0x}|^4 ds \quad (1)$$

where $E_x$ and $E_{0x}$ are the $x$ electric components of the local and background field (electric field on quartz), respectively. Fraction $f_x$ as a function of integral minor axis $\rho_{x1}$ is given in Figure S5. The effective "hotspot" area can be obtained by setting $\rho_{x1} = a$ for $f_x$(a) = 1− $e^{-5}$ (~99.3%, see Figure S5), indicating that the main SERS signal contributes from this area. Under this condition, the effective minor axis is $a$ = 18 nm. And the integrated electric field enhancement factor can be obtained according to:

$$\sqrt[4]{\frac{\int_0^{\pi ab} |E_x|^4 ds}{\int_0^{\pi ab} |E_{0x}|^4 ds}} = 17.1 \quad (2)$$