Supplemental Material

Quantum Confinement Induced Excitonic Mechanism in Zinc-Oxide-Nanowalled Microrod Arrays for UV-VIS Surface-Enhanced Raman Scattering

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**Experimental Methods**

Sample Preparation:

For the nanostructured zinc oxide (ZnO) SERS substrates, position-controlled ZnO microrod structures with nanowalls inside were grown on chemical vapor deposition (CVD) graphene films through the catalyst-free CVD process. We obtained ZnO nanowall growth selectivity by depositing an SiO$_2$ growth mask on the graphene films. The SiO$_2$ growth masks were prepared by plasma enhanced CVD (PECVD). Dimensional parameters including the height and diameter of the obtained microrods can be controlled by modifying the lithographic pattern mask or varying the growth parameters of the catalyst-free CVD process. In this work, highly oriented and ordered ZnO microrods with an outer diameter of 4 μm and a height of 5 μm were typically employed. The detailed process for growing ZnO nanostructures is described in previous reports. [1–3]

For molecule deposition, we immersed the substrates in a 4-mercaptopyridine (4-Mpy) molecular solution with a concentration of $c = 10^{-4}$ M in methanol for 2 hours, and subsequently washed the samples with deionized water.

![Figure S1](image)

**Figure S1.** (a) Schematic representation of the used sample system. The SERS substrate consists of nanostructured zinc oxide microrod arrays (black), which are shown as an SEM image in (b). (c) shows a close-up view of the ZnO-rods. As shown in (a), the SERS substrate is coated with 4-mercaptopyridine (4-MPY, yellow) for SERS measurements.
Instrument and Measurements:

Raman measurements in the UV and visible spectral range were obtained by the UT-3 Raman Spectrometer [4], which is equipped with a fully reflective custom-made entrance objective allowing an all achromatic focusing of light in the studied spectral range (see Fig. S2). Two Tsunami Ti:Sapphire laser systems, model 3950-X1BB (Spectra Physics Lasers Inc., California), which were pumped with a green Millennia Pro Xs 10sJ5 diode laser (Spectra Physics Lasers Inc., California) were used primary laser sources. The fundamental laser line was frequency doubled, tripled or quadrupled with second harmonic generation (SHG), third harmonic generation (THG) or fourth harmonic generation (FHG) (Spectra Physics Lasers Inc., California), respectively. The pulse width of the laser was monitored with an auto correlator (AC) (APE GmbH, Berlin) and around 1.7 ps. A gray filter unit enables power reduction of the laser. The laser beam was widened with a spatial filter and then focused on the sample by the main parabola of the objective also collecting the back-scattered Raman signal. Measurements at 532 nm were carried out by using a green CW Millennia laser.

For Raman measurement in the visible, we used two additional setups. Measurements at 488 nm (diode laser) and 532 nm (diode-pumped solid state (DPSS) laser) were carried out by using a McPherson 207 spectrometer equipped with a nitrogen-cooled charge-coupled-device (CCD) array detector. A LabRam HREvo 800 spectrometer and a helium-neon laser were used for the 632.8 nm measurement. The excitation power was less than 0.2 mW to avoid laser heating.

The raw Raman spectra were corrected for the spectral response of the Raman spectrometer and normalized to the used laser power and integration time [4] yielding the Raman susceptibility. The measured intensity of 4-Mpy deposited on ZnO-rods directly represents the Raman susceptibility since a monolayer of molecules was measured.
Figure S2. Schematic representation of the experimental setup for resonant Raman measurements. A Ti:Sapphire laser system (Tsunami) in combination with the UT-3 Raman spectrometer were used. The Tsunami laser was pumped with the green (532 nm) Millenia diode laser. By frequency doubling, tripling or quadrupling of the fundamental laser line, energies between 1.7 eV and 5.7 eV were obtained.

**Phonon Fitting**

The phonons were fitted with the Lorentzians according to equation (8) (main text) with wavelength and energy dependent intensities $I_{Phonon}(\omega_{inc}) = \tilde{\alpha}_i \cdot [R_i^2(\omega_{inc}) + \rho_i^2(\omega_{inc})]$. These are the wavelength dependent intensities shown in Fig. 3 in the main text. Fig. S3 shows an exemplary fit to the Raman data of 4-Mpy on the ZnO substrate as well as the bare substrate.
**Figure S3.** Raman spectrum of 4-Mpy deposited on the nanostructured ZnO substrate (red) in comparison to the spectrum of the bare ZnO substrate (blue). (a) shows the spectra in a broad range between 200 cm\(^{-1}\) and 1200 cm\(^{-1}\). In (b) fits to the data in the range between 700 cm\(^{-1}\) and 1200 cm\(^{-1}\) are shown to determine the Raman susceptibility of 4-Mpy. Please note in (a) the silicon phonon at 520 cm\(^{-1}\) and the substrate band between 200 cm\(^{-1}\) and 500 cm\(^{-1}\).

**UV SERS Enhancement Factor Estimation**

To achieve a reliable estimation, the Raman susceptibility of a monolayer of 4-Mpy adsorbed on the flat silicon dioxide (SiO\(_2\)) substrate next to the ZnO-rods was measured. The blue signal in Fig. S4(a) and (b) shows the difference between the spectrum of 4-Mpy on the SiO\(_2\) substrate and the bare SiO\(_2\) substrate. No 4-Mpy mode can be identified. In comparison, the difference between the spectrum obtained from a 4-Mpy monolayer on the ZnO-rods and the bare ZnO-rods is presented in Fig. S4(b) in red, showing clearly the 4-Mpy mode around 1000 cm\(^{-1}\). We assume a comparable monolayer formation on the ZnO-rods and the SiO\(_2\) substrate. The noise of the blue curve is presented in Fig. S4(a). The inset shows a histogram of the data points in the region of the expected 4-Mpy mode (950 – 1050 cm\(^{-1}\)), which was fitted by a Gaussian distribution. A mean Raman susceptibility of \(5.066 \times 10^{-5} \pm 5.87 \times 10^{-6}\) and a standard deviation of \(\sigma = 4.772 \times 10^{-5} \pm 5.90 \times 10^{-6}\) was found. In order to estimate the largest...
possible 4-Mpy signal in the reference measurement, we derive a maximum intensity of 2 \( \sigma \) from the noise.

From this, the smallest possible EF can be estimated as shown in eq. (S1), where \( I_{\text{SERS}} \) is the measured intensity of the ring-breathing mode of 4-Mpy adsorbed on ZnO-rods. The nanostructured ZnO-rods have a diameter of 4 \( \mu \)m, a mean height of 5 \( \mu \)m and are arranged in arrays with a spacing of 4 \( \mu \)m. Thus, the surface of the nanostructured ZnO-substrate consists of 63.3 % ZnO. With this, we found a minimal SERS enhancement factor in the UV region of about 37.8.

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EF > \frac{I_{\text{SERS}}}{2\sigma \cdot 0.633} = 37.8 \quad (S1)
\]

Alternative pathways to determine the UV-enhancement factor by measuring a sample in e.g. a cuvette did suffer from various problems such as UV-assisted sample deposition at the liquid-glass interface.

**Figure S4.** (a) Analysis of the noise of the difference spectrum of 4-Mpy on a smooth SiO\(_2\) substrate (also shown as B in (b)). The inset shows a histogram of the data points in the region of the 4-Mpy mode (950 – 1050 cm\(^{-1}\), depicted shaded in grey). A mean Raman susceptibility of 5.066 \( \cdot 10^{-5} \pm 5.87 \cdot 10^{-6} \) and a standard deviation of \( \sigma = 4.772 \cdot 10^{-5} \pm 5.90 \cdot 10^{-6} \) was found by fitting a Gaussian distribution (red line). + \( \sigma \) and – \( \sigma \) from the mean Raman susceptibility are depicted as dashed lines. (b) A (red) denotes the difference spectrum for the measurements on the ZnO-rods corresponding to Fig. 1, while B (blue) shows a reference measurement next to the ZnO-rods on the smooth SiO\(_2\) substrate. The measured positions A and B are also illustrated in the inset of (b). The black line is a guide to the eye at the mean Raman susceptibility in the area between 950 and 1050 cm\(^{-1}\) as also shown in (a).
Literature

(1) Kim, N.-J.; Kim, J.; Park, J.-B.; Kim, H.; Yi, G.-C.; Yoon, S. Direct Observation of Quantum Tunnelling Charge Transfers between Molecules and Semiconductors for SERS. Nanoscale 2019, 11, 45-49.

