Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

High-Specificity Molecular Sensing on an Individual Whispering-Gallery-Mode Cavity: Coupling-Enhanced Raman Scattering by Photoinduced Charge Transfer and Cavity Effects

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Supplementary Note I: Experimental Section

Preparation Method of the ZnO_{1-x} Cavity

To obtain high-quality WGM cavity, ZnO microrods were grown on the Si substrate via high-temperature vapor-transport method.[1] A mixture of ZnO and graphite powder with mass ratio of 1:1 was used as the reaction source. Then, the mixture was transferred into a quartz boat covered with a clean Si substrate.

Subsequently, they were placed in the center of the heating zone with a reaction temperature of 1050 °C. After reaction for 45 min, ZnO microrods were obtained on the Si substrate. Then, a single ZnO microrod was picked out and fixed on a Si substrate by epoxy resin glue. Finally, the ZnO microrod was annealed in a mixture of hydrogen and argon atmosphere at 500 °C for 120 min.

Sample Characterizations

SEM (FEI Inspect F50) equipped with an energy dispersive spectrometer was used to observe sample morphologies and conduct the element mappings. The crystal structures of samples were studied on a TEM (JEM-2100) and an XRD (Smart Lab, Cu $K_{\alpha1}$). XPS and UPS spectra were acquired on a photoelectron spectrometer (PHI 5000 Versa Probe). UV-vis spectrum was acquired from a Shimadzu UV-2600 Spectrophotometer.

Raman measurements were performed on a Jobin Yvon Lab RAM HR 800 micro-Raman spectrometer equipped with a laser source of 532 nm. Before SERS measurement, the samples were maintained in R6G solutions for 60 min and then taken out and rinsed thoroughly. The cumulative exposure time was 10 s and the laser power density was about 1.60×10^6 mW cm^{-2}.

Calculations of the Electronic Band Structure of ZnO_{1-x}

All our first principles calculations were carried out within the framework of density functional theory (DFT) as implemented in "Vienna ab initio simulation package" (VASP) [2,3] to obtain insight into the electronic properties of ZnO with point defects of oxygen vacancies. Periodic boundary conditions are used throughout the study, and the reciprocal space is sampled by a fine grid [4] of 5 × 3 × 3 k-points in the Brillouin zone. We used projector-augmented-wave (PAW) [5, 6] pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) [7] exchange-correlation approximation. Electronic wave function is expanded on a plane-wave basis set with cutoff energy of 450 eV. A total energy difference between subsequent self-consistency iterations below 10^{-5} eV is used as the criterion for reaching self-consistency. All geometries have been optimized using the conjugate-gradient method,[8] until none of the residual Hellmann-Feynman forces exceeded 10^{-2} eV/Å. The hybrid HSE06 [9] functional was used to give the more accurate band structures and band gap values with the mixing parameter α = 0.22. The point defects structure of ZnO was modeled by removing one oxygen atom from the supercell of ZnO with 32 oxygen atoms and 32 zinc atoms in our calculations. For ZnO, our procedure gives U = 4.7 eV [10] with GGA+U approach to correct for the position of the zinc d states.

Finite Difference Time Domain Simulations of the ZnO_{1-x} Cavities

To investigate the effective mode volumes and the evanescent near-field of ZnO_{1-x} cavities with different hexagonal side lengths, the FDTD is used to calculate the near-field electric field distribution of the fundamental mode confined in ZnO_{1-x} cavity. The refractive index of ZnO_{1-x} was set as 2.5 at λ = 550 nm. The hexagonal side lengths of ZnO_{1-x} cavities were set as 2, 4 and 8 μm, respectively.

Supplementary Note II:

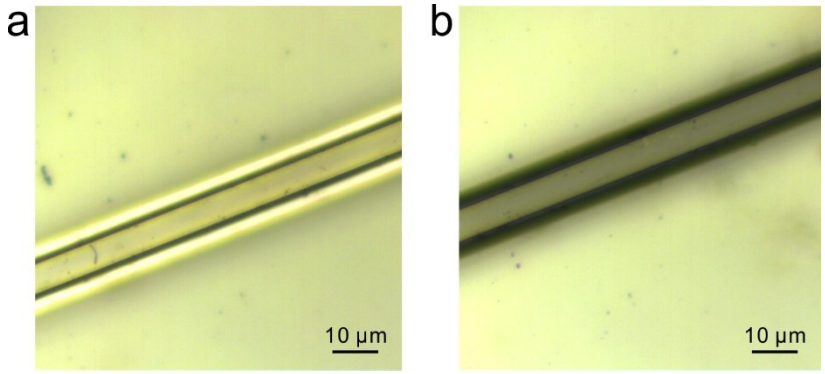

Figure S1. Optical images of two reference samples. (a) Stoichiometric ZnO microrod (ZnO cavity) with WGM. (b) Nonstoichiometric ZnO_{1-x} microrod without WGM.

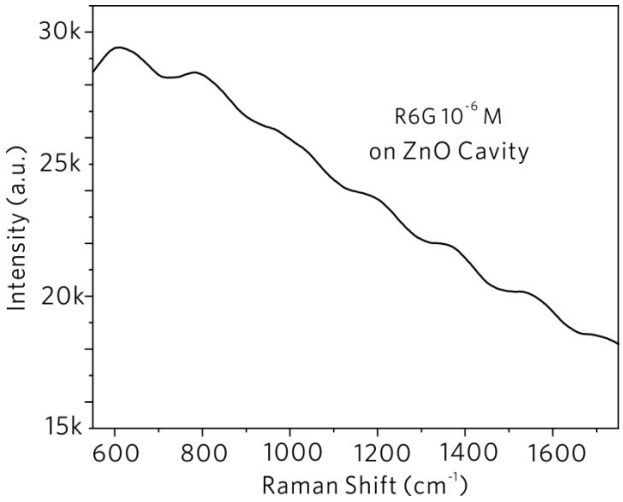

Figure S2. Raman spectrum of R6G (10^{-6} M) collected from ZnO cavity (reference sample). No Raman mode of R6G molecule could be observed.

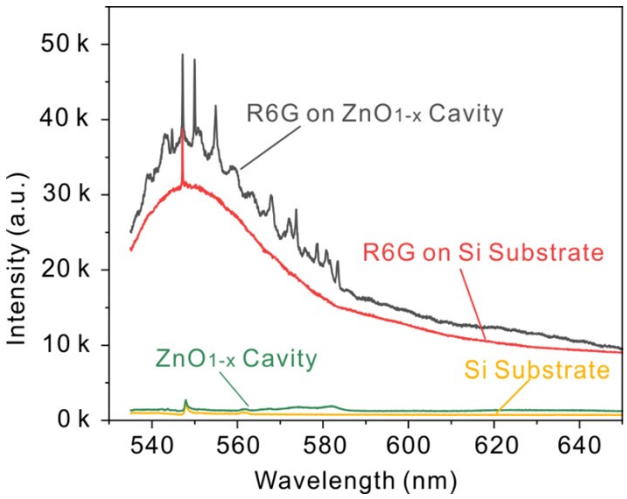

Figure S3. Photoluminescence (PL) spectra collected from bare Si substrate, ZnO_{1-x} cavity, Si substrate with R6G adsorption, and ZnO_{1-x} cavity with R6G adsorption. The results confirm that the bare ZnO_{1-x} cavity shows no PL emission, and the light confined in the ZnO_{1-x} cavity should come from the adsorbed R6G molecules.

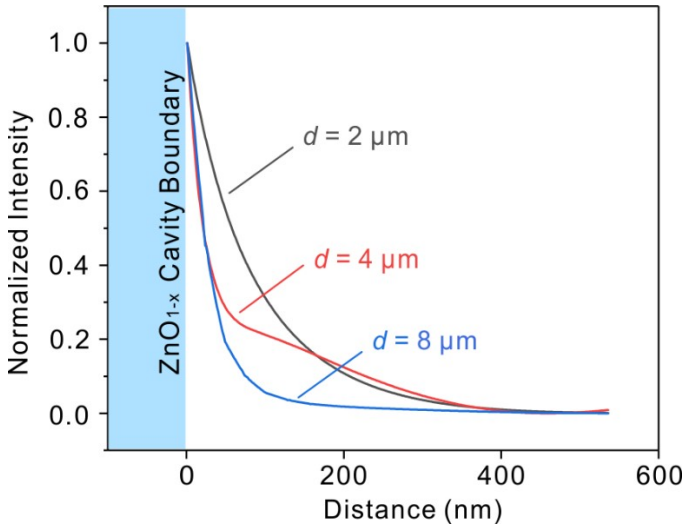

Figure S4. Evanescent fields at the outside of ZnO_{1-x} cavity walls.

Calculation of Raman Enhancement Factors

The Raman enhancement factors (EFs) are calculated according to the following formula:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{normal}/N_{normal}} \quad \text{(S1)}$$

$$N_{SERS} = \frac{CVN_A A_{Raman}}{A_{Sub}} \quad \text{(S2)}$$

$$N_{normal} = \frac{\rho h A_{Raman} N_A}{M} \quad \text{(S3)}$$

I_{SERS} and I_{normal} are the intensities of the selected Raman peak in SERS spectra and normal Raman spectra, respectively. N_{SERS} and N_{normal} are the number of molecules in the testing area of SERS and normal Raman measurements, respectively. The data of bulk R6G is used as normal Raman spectrum reference. For the SERS measurement, the intensity is obtained by taking average from measurements of 10 random spots, and the number of molecules is estimated by equation (S2) on the assumption that the molecules are distributed uniformly on the substrate. *C* is the molar concentration of R6G solution. N_A is Avogadro constant. A_{Raman} is the laser spot area. A_{Sub} is the effective area of the substrate, which is approximately $\pi/4\ cm^2$. The confocal depth h of the laser beam is ~ 21 μm. The molecular weight *M* of R6G is 479 g mol^{-1} and density ρ of bulk R6G is 1.15 g cm^{-3}.

The Raman EFs of ZnO_{1-x} and ZnO_{1-x} cavity are estimated to ~ 6.65×10^4 and 1.47×10^6 at the R6G concentration of 1.0×10^{-6} M, respectively.

References

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