ELECTRONIC SUPPORTING INFORMATION

ZORRO: Zirconium Oxide Resonators for All-in-One Raman and Whispering-Gallery-Mode Optical Sensing

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ESI 1 - Experimental

ZORRO Fabrication

ZORRO beads consist in core/shell SiO_2/ZrO_2 beads. Monodisperse (nominal diameter: 2.06±0.05 μm) SiO_2 core beads were purchased by microparticles GmbH® were placed onto a (1 0 0) crystalline Si wafer in a single sphere configuration (using a droplet of 10 μL of 0.05 mg/mL concentration). These silica cores were then coated with a conformal layer of zirconia through atomic layer deposition (Savannah 100 ALD flow reactor, Cambridge Nanotech Inc.®). In particular using tetrakis(dimethylamido)zirconium (TDMAZ Sigma Aldrich®) as zirconium source and MilliQ water as oxygen source. The temperature and pressure of the deposition were 200°C and 0.5 Torr, respectively. TDMAZ (99.999%) and H_2O were evaporated from stainless-steel containers (TDMAZ preheated at 85°C). Nitrogen 6.0 was used for conveying the precursors inside the deposition chamber and subsequent purging. Each ALD cycle consisted in pulsing TDMAZ (0.25 s), purging with N_2 (10 s), pulsing H_2O (0.015 s) and purging with N_2 (15 s). The deposition rate was 0.06993 nm/cycle, confirmed with XRR measurements (D8-Advance diffractometer purchased by Bruker GmbH) equipped with a Göbel mirror.

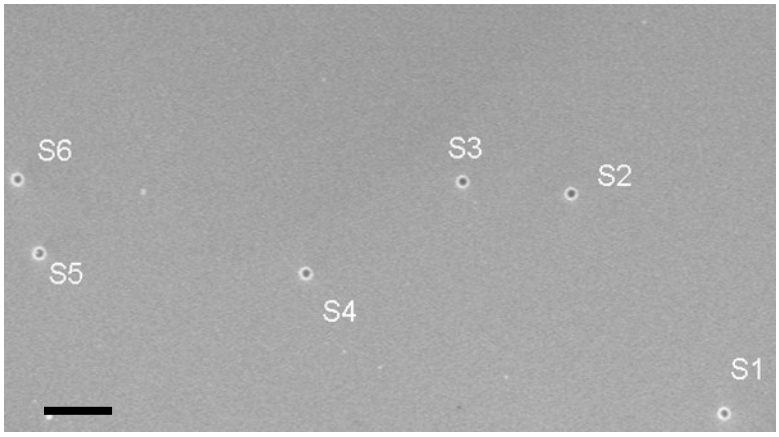

Figure ESI 1. SEM micrograph showing the distribution of selected ZORRO beads (S1-S6) on a silicon substrate. Scale bar: 10 μm.

MicroRaman

The μ-Raman measurements were performed in backscattering configuration using a Labram HR-800 by Horiba-Jobin Yvon® provided with optical microscopes (BX41; Olympus Optical Co. Ltd.) equipped with a 632.81 nm HeNe laser (5 mW of maximum power on the sample surface) and a Silicon CCD (Wright Instruments Ltd.).

All the measurements were repeated up to 10 times. The measurements were carried out using both a 600 and a 1800 l/mm gratings with acquisition times ranging from 10 s. The baseline of the spectra was corrected with Labspec 5.0 software.

WGM sensing of thin films

TiO_2 and ZnO have been deposited on ZORROs surface by ALD. In the case of titanium dioxide, tetrakis(dimethylamido)titanium (TDMAT Sigma Aldrich®) and MilliQ water were utilised as titanium and oxygen source, respectively. The temperature and pressure of the deposition were 90°C and 0.5 Torr, respectively. TDMAT (99.999%) and H_2O were evaporated from stainless-steel containers (TDMAT pre-heating: 85°C). Nitrogen 6.0 was utilised for conveying the precursors inside the chamber and purging. The ALD recipe cycle consisted in a 0.1s pulse of TDMAT, 10 s N_2 purging, 0.015 s pulse of H_2O and a 8 s purging with N_2. The deposition rate was 0.06830 nm/cycle, confirmed by XRR measurements.

For zinc oxide, diethylzinc (DEZ Sigma Aldrich®) and MilliQ water were utilised as zinc and oxygen source, respectively. The temperature and pressure of the deposition were 150°C and 0.5 Torr, respectively. DEZ (99.999%) and H_2O were evaporated from stainless-steel containers at room temperature. Nitrogen 6.0 was used for carrying the precursors inside the chamber and purging. The ALD recipe cycle consisted in a 0.015 s pulse of DEZ, 7s purge with N_2, 0.015 s pulse of H_2O and a 7 s purge with N_2. The deposition rate was 0.1470 nm/cycle, confirmed by XRR measurements.

CB[7]-MB recognition

The Raman spectrum of bear ZORRO beads deposited onto a Si substrate was acquired as a reference (main text: Fig. 3, step I). Then a 10 μL aqueous solution of Cucurbit[7]uril (CB[7]) 10^{-5} M was drop-casted onto the ZORRO substrate and naturally dried at room temperature. Then the sample was generously rinsed in MilliQ water to remove any possible excess of CB[7] molecules and a second set of measurements were performed (main text: Fig. 3, step II). 10 μL of an aqueous solution of Methylene Blue (MB) 10^{-5} M were drop-casted onto the ZORRO-CB[7] substrate and naturally dried at room temperature. The third set of measurements (main text: Fig. 3, step III) was carried out. The sample was generously rinsed in MilliQ water to remove any MB molecule not complexed by CB[7] and a fourth set of measurement was run (main text: Fig. 5, step IV). The Methylene Blue (MB) and Cucurbit[7]uril powders utilised to prepare the solutions were purchased by Sigma Aldrich®.

ESI 2 – Finite Element Analysis

The Finite Element Analysis of the optical properties of a ZORRO bead was carried out using Comsol Multiphysics 5.2 (Comsol Inc., Burlington, MA). The modeled geometry consists in a free-standing silica sphere of 1.05 μm radius, covered by a 100 nm thick ZrO_2 film. Silica refractive index was set to 1.45 while ZrO_2 refractive index was taken from Wood *et. al.* [1]. The system was excited with a plane electromagnetic wave and the power response was observed. None electric field intensity dependence of ZrO_2 refractive index was considered. The electromagnetic problem was solved for the electric field in the frequency domain, using a quadratic discretization for each mesh element.

The mesh was chosen in order to always ensure computational convergence. In the ZrO_2 film, the minimum element size was kept constant at 25 nm. For the silica core the minimum element size was chosen as wavelength/($n_{SiO_2} \cdot 10$). A linear stationary iterative solver was used as algorithm to solve the finite element problem.

The scattering cross section was obtained calculating the surface integral of the outgoing time averaged power-flow and weighting it by the exciting power-flow. The formal expression is

$$\sigma_{sc} = \frac{1}{S_{in}} \int_S x \cdot P \, ds$$

where S is the sphere surface, $x = [x,y,z]\ [m]$ is the position vector, $P = [P_x,P_y,P_z]\ \left[\frac{W}{m^3}\right]$ is the Poynting vector and $S_{in} = {E_0^2}/{2 \cdot Z_0}\ \left[\frac{W}{m^2}\right]$ is the incident power-flow. The absorption cross section was calculated integrating over core-shell volume the time average dissipated power density, weighted by the incident power-flow. The formal expression is:

$$\sigma_{abs} = \frac{1}{S_{in}} \int_V Q_e dv$$

where V is the volume,

$$Q_e = \frac{1}{2} Re\left\{ \frac{\omega \varepsilon''(\omega)}{4\pi} E \cdot E^* \right\} + \frac{1}{2} Re\{ i\omega\mu(\omega) H \cdot H^* \}$$

where E, H are the complex exciting electric and magnetic fields while ε'', μ are the imaginary parts of dielectric and magnetic permeability constants.

Finally, the extinction cross-section was obtained summing scattering and absorption cross-sections.

$$\sigma_{ext} = \sigma_{sc} + \sigma_{abs}$$

[1] Wood and Nassau 1982, *Applied Optics* Vol. 21, Issue 16, pp. 2978-2981(1982).

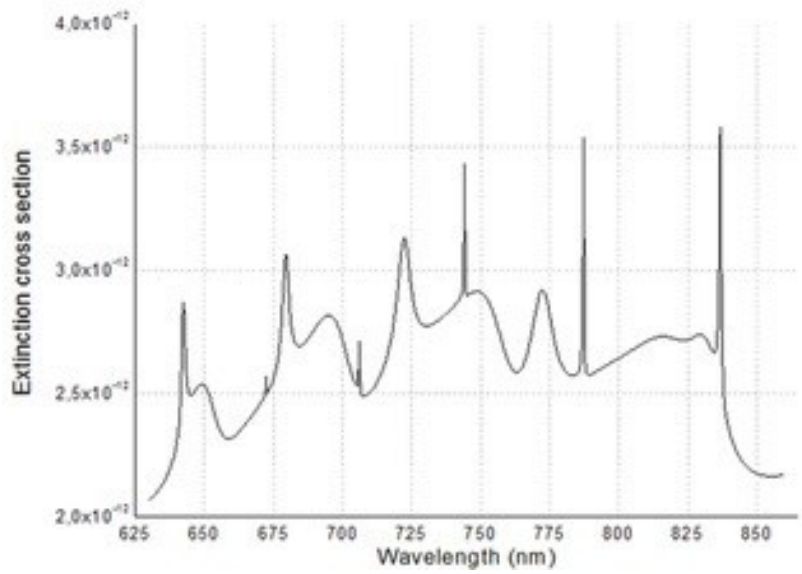

Figure ESI2 a. Extinction cross-section of a free-standing ZORRO bead.

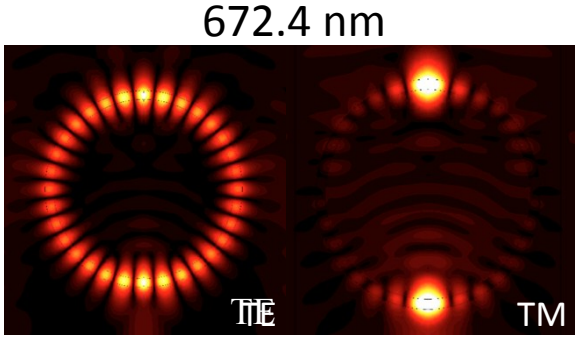

Figure ESI2 b. Distribution of the electric field (intensity integral) on the surface of a free-standing ZORRO sphere surface for a selected wavelength corresponding to a WGM (TE and TM).