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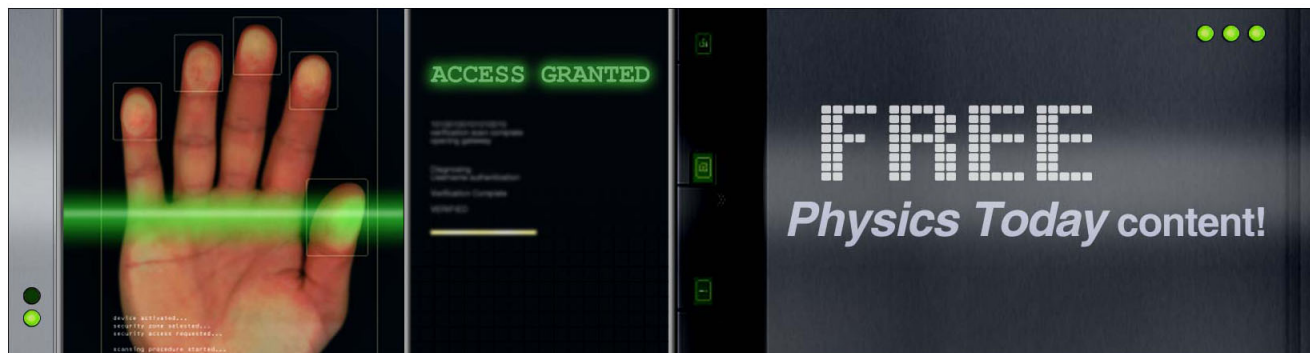
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Interfacial refractive index sensing using visible-excited intrinsic zinc oxide photoluminescence coupled to whispering gallery modes

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Whispering gallery modes (WGMs) excited by the intrinsic photoluminescence (PL) in zinc oxide microspherical resonators are investigated in this work. The microspheres were synthesized via a one-pot hydrothermal technique. A polymer was applied after the synthesis to fill remaining pores in the oxide particle. Defect-related ZnO PL was excited in the visible, coupling to WGMs. The observed WGMs red-shift with increasing refractive index of the surrounding medium with a sensitivity of 90–100 nm/refractive index unit. The spherical microresonators may be used to investigate binding to and structure at the particle/solution interface. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4817273>]

One of the challenges in interface science is the characterization of the interface between suspended particles and surrounding medium. In the last decade, vibrational sum frequency scattering^{1–3} and ellipsometric light scattering^{4–6} have been established as new experimental techniques for submicrometer particles. In the μm size regime, light can be trapped inside particles; resonance conditions for total internal reflection at the curved particle/medium interface lead to the occurrence of whispering gallery modes (WGMs), the shift of which has been used for detection of adsorbing species.^{7–12} Wavelength and strength of WGMs depend on particle radius a , refractive indices n_s of particle, and n_e of surrounding medium.¹³ The evanescent field produced, when WGMs occur, extends into the sphere's environment, and probes change in the surrounding medium near the interface.^{9,10} The vacuum wavelength λ of a WGM resonance, and the quality factor $Q = \lambda/(\Delta\lambda)$, where $\Delta\lambda$ denotes the full width at half maximum of the resonance peak, are quantities sensitive to the local refractive index in the vicinity on the particle. In most systems using WGMs, light is coupled into the microresonator through an intimate contact with an evanescent wave,^{7,11} or by placing a local light source, e.g., based on fluorescent dyes or quantum dots (QDs), within the microresonator.^{12,14,15} A promising material for developing microresonators is the wide band gap semiconductor ZnO, a material with low toxicity and high biocompatibility.¹⁶ Various forms of ZnO optical microresonators, such as disks,^{17–19} rods or wires,^{20,21} and spheres,^{22,23} have been studied, mainly for lasing applications. The use of spherical isotropic structures has the advantage to overcome the optical loss at corners, as total reflection can be obtained in all directions.^{18,24}

In this letter, we report a refractometric sensor exploiting the strong intrinsic green luminescence of ZnO,²⁵ which can be excited with visible light,²⁶ in microsphere resonators.

ZnO microspheres with $a \approx 2\text{--}4\ \mu\text{m}$ were synthesized via a hydrothermal growth technique.²³ The ZnO particles were washed several times with ultrapure water and then with ethanol. Then, the particles were collected in a glass

vial by centrifugation. Subsequently, the particles were annealed for 12 h at 450 °C in ambient atmosphere. Finally, annealed ZnO particles were suspended in ethanol and kept at 4 °C until used. A fraction of the particles were exposed to a UV crosslinking polymer adhesive to fill pores present after the synthesis. The polymer treatment was done by dipping the prepared sample into 1 wt. % of Norland Optical Adhesive 81 (specified refractive index after curing: 1.56) in acetone for 20 min, and subsequent developing under UV illumination for 5 min. The resulting polymer has no light absorption in the spectral window of interest. Fig. 1(a) shows scanning electron micrographs (SEM; Zeiss LEO 1550 VP) of the ZnO particles, with an image of a polymer-treated sphere (inset). Elemental analysis, performed using energy-dispersive X-ray spectroscopy (EDX; Oxford Instruments), shows the purity of the ZnO particles [Fig. 1(b)]. The X-ray diffraction pattern [XRD, Bruker-AXS D8 with Cu-K α source; Fig. 1(c)] shows their crystallinity and phase purity.

For preparation of samples for optical measurements, a drop of the particle suspension in ethanol was placed on a glass cover slip and dried in an oven. The particles were physically attached to the glass substrate by quickly swiping a hydrogen flame four or five times over the sample and allow it to cool. The attached particles were stable and did not wash out during experiments. The particle-containing cover slips were fixed in a custom-made flow cell for liquid environments [Fig. 2(a)]. Ethanol-water mixtures were prepared with the following weight fractions of ethanol: 0.10, 0.20, 0.30, 0.40, and 0.50. The refractive indices of the mixtures are 1.3395, 1.3469, 1.3535, 1.3583, and 1.3616, respectively.²⁷ These mixtures were consecutively delivered to the sample compartment using a peristaltic pump. Each solution was flown through the cell for at least 10 min. Subsequent photoluminescence (PL) measurements were carried out without flow at room temperature in a backscattering geometry using a commercial confocal Raman microscope (Horiba Jobin Yvon LabRAM, France) with an excitation at 514 nm by an Ar⁺ laser (20 mW output). The laser was focused onto a single ZnO particle using a 50 $\times$ long working distance objective (Olympus; NA = 0.5). Backscattered light was collected through the same objective, the excitation wavelength filtered

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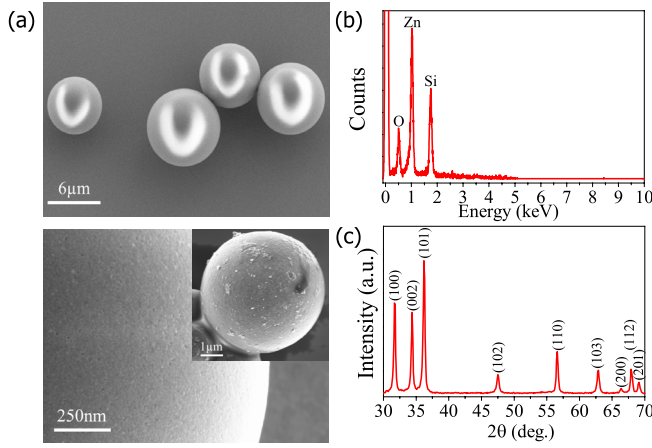


FIG. 1. (a) SEM (inset: polymer-treated particle) and (b) EDX analysis of ZnO particles placed on a Si wafer. (c) XRD pattern measured from a collection of particles placed on a glass substrate.

out by an edge filter, and the light at higher wavelengths was directed onto a CCD detector via a grating of 600 grooves mm^{-1} . Resulting separation between neighboring points in the spectrum was $1/8 \text{ nm}$. All spectra were acquired for 20 s using a $500 \mu\text{m}$ confocal pinhole. Fig. 2(b) shows an optical micrograph of a single ZnO particle on a glass substrate immersed in a liquid and (c) the corresponding PL map.

PL spectra are shown in Fig. 3(a). The luminescence caused by absorption of the excitation wavelength through defect states in the ZnO particles couples to the resonator's WGMs, resulting in periodic sharp resonance peaks of WGM in the PL spectra. (In addition to PL, the spectra show two emissions centered at 605 and 625 nm. These peaks correspond to the Raman CH stretching modes and OH stretching modes, respectively. These modes are not discussed in this work.) The WGMs in a spherical microcavity are characterized by a set of quantum numbers that describe the

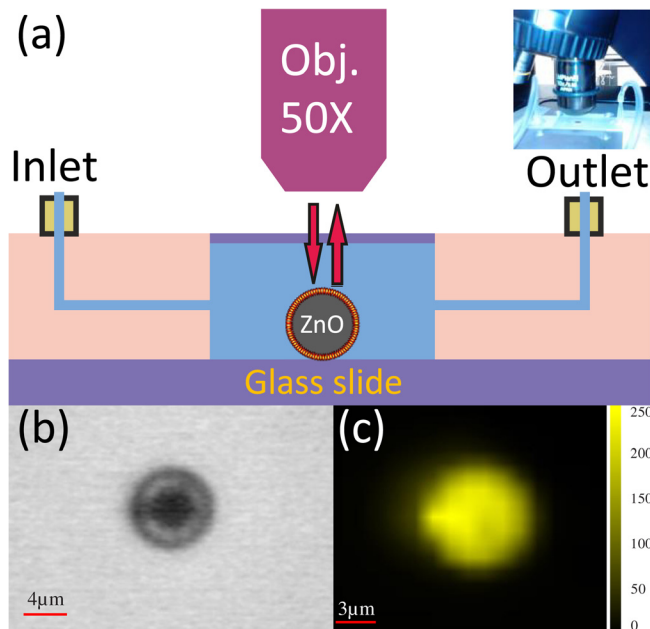


FIG. 2. (a) Schematic layout and photographic image (inset) of the experimental setup. (b) Optical micrograph and (c) PL map of a ZnO particle on a glass substrate.

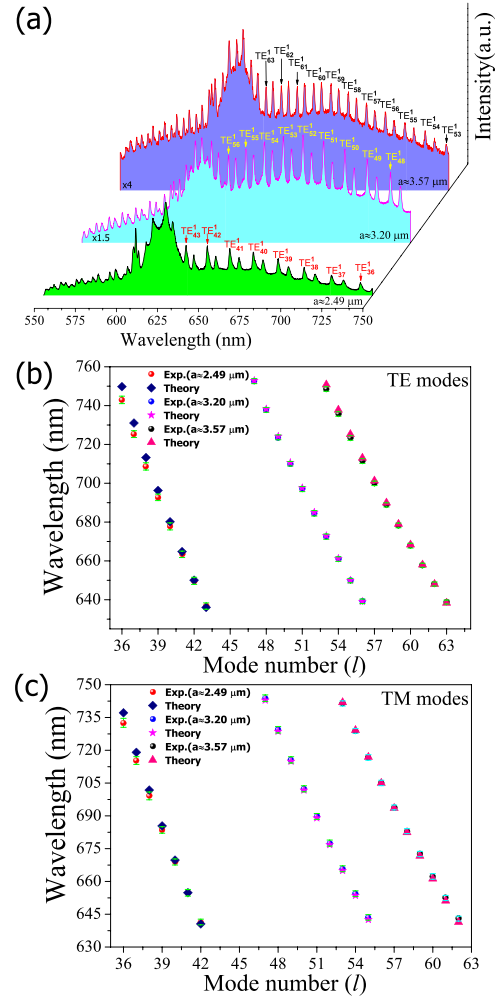


FIG. 3. (a) PL spectra of ZnO particles [$a = (2.488 \pm 0.006) \mu\text{m}$, $(3.199 \pm 0.006) \mu\text{m}$, and $(3.569 \pm 0.006) \mu\text{m}$] in medium with $n_e = 1.3469$. Comparison between experimental and theoretical λ for (b) TE and (c) TM polarization.

angular order l and radial order i . While l corresponds to the number of field maxima around the surface of the sphere between polar angles 0° and 180° , i describes the number of field maxima in the radial direction.²⁸ Assuming $a \gg \lambda$, the relation between size parameter $x_l^{(i)} = 2\pi a/\lambda$ and l as well as i can be expressed as a power series in $\nu = l + 1/2$ as²⁹

$$n_s x_l^{(i)} = \nu + \frac{\alpha_i}{2^{1/3}} \nu^{1/3} - \frac{mp}{\sqrt{m^2 - 1}} + \frac{3\alpha_i}{10 \cdot 2^{2/3}} \nu^{-1/3} + \frac{m^3 p (2p^2/3 - 1) \alpha_i}{2^{1/3} (m^2 - 1)^{3/2}} \nu^{-2/3} + O(\nu^{-1}), \quad (1)$$

where $m = n_s/n_e$, and $p = 1$ for TE or $p = 1/m^2$ for TM polarization. The i th zero of the Airy function is denoted as α_i .

Using Eq. (1), WGM mode numbers can be assigned to the measured resonance peaks [Fig. 3(a)], enabling a precise determination of a . To simplify the problem, n_s of ZnO was considered constant as 1.9799 within the spectral range of 635–750 nm,³⁰ assuming that the dispersion of <0.015 has negligible influence on the results. A close agreement is found between the calculated and observed WGM resonance wavelengths for both TE- [Fig. 3(b)] and TM-polarization [Fig. 3(c)]. From the measurement and analysis presented in

Fig. 3, a for the respective spheres was found to be $(2.488 \pm 0.006) \mu\text{m}$, $(3.199 \pm 0.006) \mu\text{m}$, and $(3.569 \pm 0.006) \mu\text{m}$. The error estimates δa used here were obtained as $\delta a = \sqrt{(\partial\lambda/\partial a)^{-2}(\Delta\lambda)^2}$. Here, $(\partial\lambda/\partial a)$ was determined numerically for the modes used in the analysis from Eq. (1), and was found to be very similar for all modes. Only first radial order ($i=1$) was considered, because the mode with higher i is less sensitive to the surrounding environment.³¹ The corresponding WGMs are assigned as TE_l^1 or TM_l^1 .

A comparison for the same particle between a determined from WGMs and a determined from SEM yields information about the fraction of air in the particle. Examination of particles yielded no visible difference in a . Considering an error ~ 20 nm, using the Maxwell-Garnett relation, the fraction of air in the porous particles is found to be <1 vol. %. Thus, the effect of porosity on n_s has been neglected.

In a subsequent experiment, WGM stability with time was investigated of both polymer-treated as well as untreated particles in ethanol-water mixtures. Corresponding spectra are shown in Fig. 4(a). No peak shifts of WGMs are observed for both kinds of particles, indicating the stability of the ZnO particles in the environments used on the time scale of the experiment. The observed decrease in Q is attributed to photocorrosion, because it is related to the time the particles are illuminated and not to the time the particles are immersed. Both kinds of particles were immersed in mixtures of different n_e [cell in Fig. 2(a)]. As opposed to previous reports,⁷⁻¹² the WGMs of ZnO particles as prepared show a blue-shift when changing n_e from 1.3395 to 1.3616, which coincides with a decrease in Q . The sensitivity $s = |\Delta\lambda/\Delta n|$ of the blue shift was found to be, e.g., $s = (148 \pm 8)$ nm/RIU (RIU-refractive index unit) for the

TE_{55}^1 mode of a particle with $a = (3.199 \pm 0.006) \mu\text{m}$. However, on reverting n_e to the original 1.3395, the blue shift continues, showing that the shift is not alone caused by the changing n_e . A blue-shift during exposure to air of WGMs in porous Si particles has been attributed to the oxidation of the Si, and the consequent decrease in the effective n_s .³² The blue-shift here is attributed to reorganisation processes within the slightly porous [Fig. 1(a)] ZnO particles. Control experiments show a blue-shift of the WGMs with time when purging the cell with a single solvent, indicating that the dissolution equilibrium of ZnO and the subsequent removal of traces of Zn^{2+} is responsible for the observed blue-shift: though no damage of the particles is visible after ~ 1 h of treatment, the slight loss of material effectively decreases n_s .

While the observed shift shows the potential of WGMs in the study of interfacial phenomena, it implies limits in sensing. To overcome the problem, polymer treatment was applied. Fig. 4(b) shows the spectra of a polymer treated ZnO particle exposed to different ethanol-water mixtures with varying n_e . The typical red shift in the WGMs was observed with increasing n_e ,⁷⁻¹² which is now reversible. The strength of the WGMs depends on the treatment time with polymer, as the polymer may form layers of different thicknesses around the particles after extended treatment. For the treatment time applied here, no homogeneous layer is visible by SEM, so the thickness can be few nm at maximum.

Fig. 4(c) shows a comparison between experimental λ of polymer treated particles with $a = (3.391 \pm 0.003) \mu\text{m}$ and values calculated for pure ZnO particles in a medium with $n_e = 1.3616$. In the calculation, a homogeneous ZnO particle with a single n_s was used to simplify the problem. The calculated λ agrees well with the experimentally

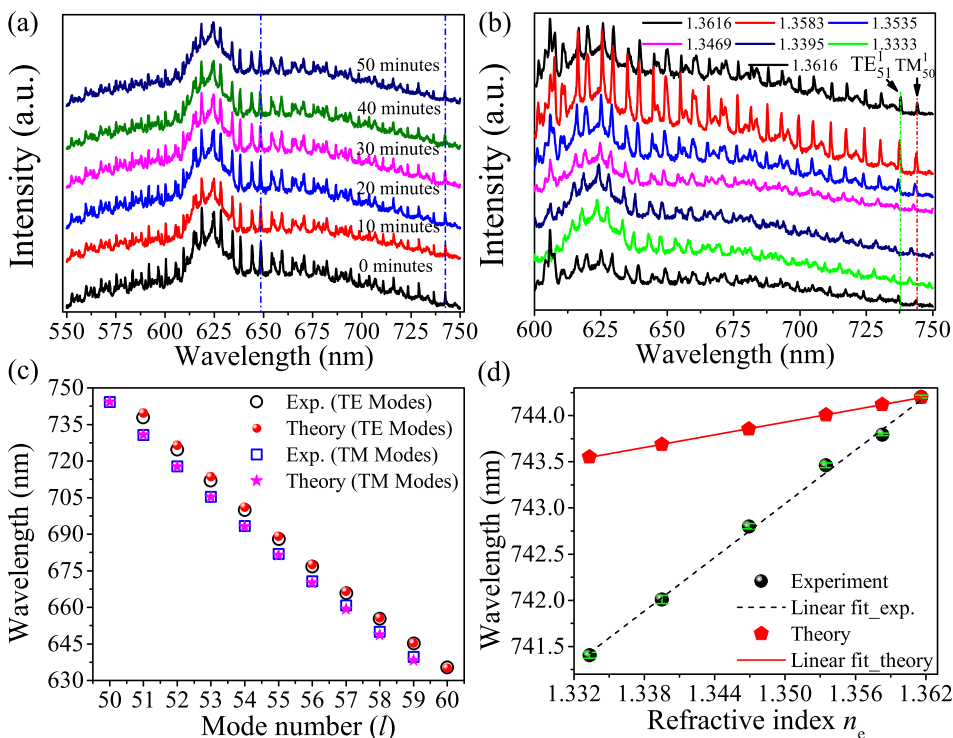


FIG. 4. (a) Time-dependent PL spectra of a ZnO particle in an ethanol-water mixture of $n_e = 1.3425$, (b) PL spectra of a ZnO particle in different ethanol-water mixtures with n_e as indicated in the graph. (c) Experimental and theoretical λ of WGMs for a polymer-treated ZnO particle of $a = (3.391 \pm 0.003) \mu\text{m}$ exposed to a medium of $n_e = 1.3616$. (d) WGM peak as function of n_e for TM_{50}^1 mode. Error bars are smaller than the symbols and represent the standard deviations of λ obtained from fitting the spectra to a Gaussian peak.

observed. Fig. 4(d) shows the shifting of the TM_{50}^1 mode with n_e . From the graph in Fig. 4(d), $s = (96 \pm 3)$ nm/RIU. Based on a calculation using Eq. (1), $s = 22$ nm/RIU. Similarly, for the TE_{51}^1 mode, $s = (94 \pm 3)$ nm/RIU from experiment, and 14 nm/RIU from calculation (not shown). As observed for incorporated QDs,¹² the experimentally observed sensitivity is significantly higher than the theoretical value. For incorporated QDs, the sensitivity enhancement has been attributed to a modal location nearer to the particle's surface due to the high refractive index of the QDs.¹² Such an explanation is unlikely in the current case. Here, the internal structure of the particles may play a role as well. The optical anisotropy of ZnO and deviations for this in the derivation of Eq. (1) may also contribute. A thorough investigation is needed, involving full Mie computations and well-defined particles, to understand the cause of the deviations. While s reported here is lower than for the particles incorporating QDs,¹² s is higher compared with a prism coupled silica microsphere resonator.⁷ While this work focused on the demonstration of the overall properties, adsorption studies and use of the WGM resonators for detailed investigation of the interface structure are ongoing.

In summary, this work introduces ZnO-based microspherical resonators for refractometric sensing by investigating the WGM shift. The intrinsic green luminescence of ZnO couples to the microresonator's WGMs. The ZnO particles needed can be prepared in a simple, one-pot synthesis from cheap starting materials, and do neither require sophisticated coupling schemes, nor expensive light sources. By monitoring the WGM shift of a polymer-treated ZnO microsphere with changing refractive index in the surrounding medium, a sensitivity of ≈ 100 nm/RIU was achieved. High sensitivity studies of chemical processes on ZnO surfaces may be enabled by the microresonator used here. For this reasons, alternatives to the polymer treatment, e.g., by using SiO_2 , are under investigation. As oxidic surfaces are mostly terminated by $-OH$ groups, they can be readily functionalized. The particles can be easily integrated with existing microfluidic systems for developing miniaturized multiplex label free optical sensing platforms.

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