Spectral tuning of liquid microdroplets standing on a superhydrophobic surface using electrowetting

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Using electrowetting, we demonstrate reversible spectral tuning of the whispering gallery modes of glycerol/water microdroplets standing on a superhydrophobic surface by up to 4.7 nm at 400 V. Our results can inspire electrically tunable optical switches and filters based on microdroplets on a superhydrophobic surface. The sensitivity of the observed spectral drift to the contact angle can also be used to measure the contact angles of microdroplets on a superhydrophobic surface. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2927373]

Optical communication systems require largely tunable optical microcavities to function as building blocks of largely tunable optical switches and filters.[1] Liquid microdroplets standing on a superhydrophobic surface possess unique features which can make them technologically favorable in such applications. First, due to their liquid nature, these microdroplets are easily deformable.[2,3] Second, thanks to the superhydrophobic surface, their position stabilization is granted. They do not require complex position stabilization techniques such as electrodynamic levitation[4] or optical tweezing.[5] Third, they are cost effective and disposable. They do not pose any microfabrication challenges. Fourth, the interaction of these microdroplets with the superhydrophobic surface inspires unique shape deformation mechanisms. To this end, here we demonstrate spectral tuning using electrowetting.

Electrowetting is the increase in the wetting of a superhydrophobic surface by conducting liquid microdroplets due to an external electric field.[6] As a result of an applied voltage, a space charge layer of counter ions is built near the superhydrophobic surface in the microdroplet. This leads to a decrease in the effective solid-liquid interfacial tension which in turn decreases the contact angle. Electrowetting has recently become a powerful tool in microfluidics research inspiring various important applications including lab-on-a-chip devices in which microdroplets are translated along arbitrary paths,[7] adjustable microlenses,[8] and electronic displays.[9] In this letter, we report the spectral tuning of the whispering gallery modes (WGMs) of glycerol/water microdroplets standing on a superhydrophobic surface using electrowetting. The decrease in the contact angle leads to an increase in the equatorial radius of the microdroplets resulting in the redshift of the WGMs which circulate in the equatorial plane parallel to the surface. We demonstrate spectral tuning by up to 4.7 nm as a result of a maximum applied voltage of 400 V. We also show that the observed spectral tuning mechanism is reversible.

The sketch of the experimental setup is shown in Fig. 1. Two cover glasses having conducting, indium tin oxide (ITO) coatings on one of their surfaces were used in the sample chamber. The nonconductive surface of one of the cover glasses was spin coated with hydrophobically coated silica nanoparticles (Degussa A.G., LE2) using a 50 mg/ml

ethanol dispersion. Glycerol/water microdroplets were sprayed onto the superhydrophobic surface using an ultrasonic nebulizer from a 10/90 glycerol/water solution containing 5 μM rhodamine B and 135 mM KCl. Water content in the microdroplets quickly evaporated on the superhydrophobic surface under ambient temperature and pressure and a relative humidity of ~40%, revealing microdroplet diameters ranging from a few up to ~20 μm with resulting glycerol contents >90%. Following microdroplet generation, the second cover glass was glued on the first cover glass with its ITO coated surface facing the superhydrophobic surface. The spacing between the two cover glasses was kept at minimum by squeezing during the sealing of the chamber. After the adhesive was hardened, spacings of $d_1=30-60$ μm were typically obtained, and the chamber between two cover glasses was totally sealed. All the data presented in this letter were taken from microdroplets in the same sample chamber with a spacing of $d_1=40$ μm. In all results presented, a positive voltage was applied between nodes A and B, ($V_{AB} \geqslant 0$). Similar spectral shifts in the WGMs were observed as a function of $|V_{AB}|$ for all microdroplets when the sign of V_{AB} was reversed. Spectral positions of the WGMs were determined with fluorescence spectroscopy experiments. Individual microdroplets were excited in the vicinity of their rims with a green, solid state laser ($\lambda=532$ nm) using an air objective
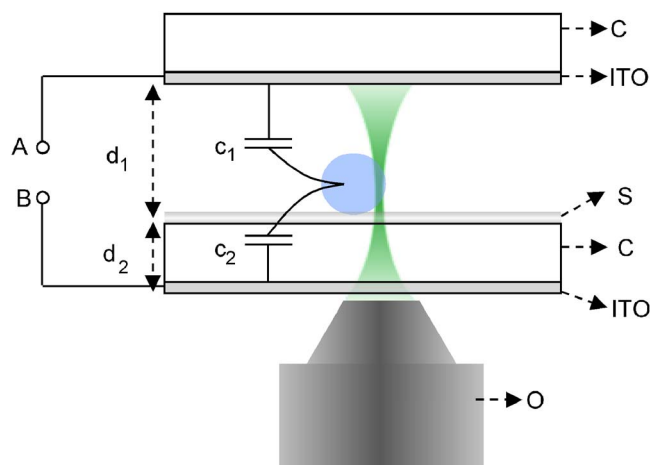

FIG. 1. (Color online) Illustration of the experimental setup. C, cover glass; S, superhydrophobic coating; ITO, indium tin oxide coating; O, microscope objective. The sketch is not to scale. c_1 and c_2 indicate capacitances per unit area.

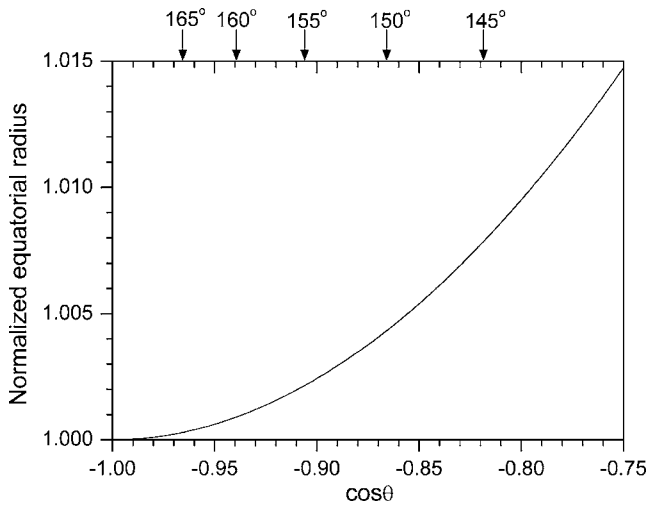a)Electronic mail: akiraz@ku.edu.tr.

FIG. 2. Normalized equatorial radius vs cosine of the contact angle of an ideal truncated sphere with constant volume. Contact angles are indicated with arrows.

(NA=0.8, 60×) in the inverted geometry. Fluorescence signal was collected using the same microscope objective, transmitted through a dichroic mirror and a 1.5× magnification element, and dispersed using a 0.5 m monochromator before detection by a charge coupled device camera (spectral resolution: 0.15 nm). An exposure time of 0.5 s was used to record the fluorescence spectra.

The characteristic signature of electrowetting is the parabolic dependence between the cosine of the contact angle ($\cos \theta$) and the external voltage applied between a conducting droplet and a conducting layer lying below a superhydrophobic surface, separated by an insulating layer (U):

$$\cos \theta = \cos \theta_Y + \frac{\varepsilon_0 \varepsilon_d}{2d\sigma_{lv}} U^2.$$

In this equation, θ_Y, ε_0, ε_d, σ_{lv}, and d denote the Young's equilibrium contact angle, permittivity of free space, dielectric constant of the insulating layer, liquid-vapor interfacial energy, and the thickness of the insulating layer, respectively. In our experimental configuration, the voltage is not directly applied between the microdroplet and the conducting layer. Applied voltage (V_{AB}) and the actual potential difference between the microdroplet and the conducting layer underneath (U) are related as $U=V_{AB}c_{eq}/c_2$, where c_1 and c_2 (shown in Fig. 1) denote capacitances per unit area, and $c_{eq}=c_1c_2/(c_1+c_2)$ is the equivalent capacitance per unit area.

In Fig. 2 we plot the dependence of the equatorial radius (r, normalized to 1 for the ideal sphere) of an ideal truncated sphere to $\cos \vartheta$ considering that the volume is kept constant. A linear approximation to this curve can be made assuming small changes in the contact angle. Furthermore, for large mode numbers, a linear asymptotic relationship exists between the spectral position of the WGMs (λ) and r.[10] As a result, a parabolic relationship can be expected between λ and V_{AB}, for small changes in the contact angle. Assuming an unbiased (under 0 V) contact angle of 150°, the following relationship is obtained:
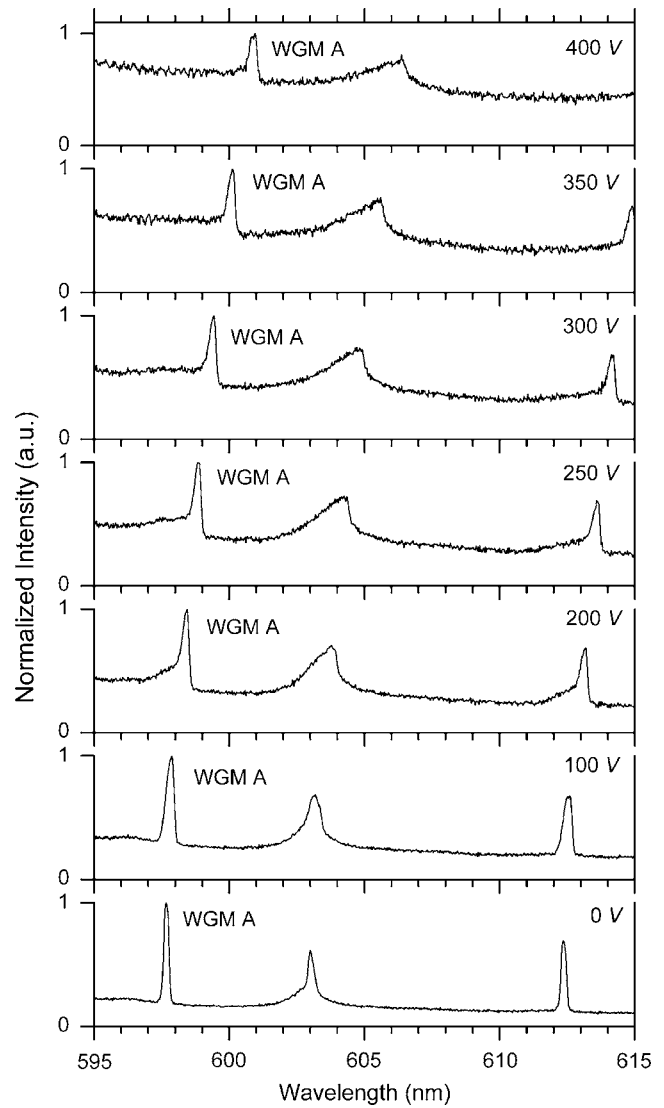

FIG. 3. Normalized emission spectra recorded from a 6.5 μm diameter microdroplet while the voltage is gradually increased from 0 to 400 V. At 400 V a maximum redshift of 3.3 nm is observed in the WGM A. At high voltages, a blue shoulder is seen in the WGMs.

$$\lambda = \lambda_0 + 0.032\lambda_0 \frac{\varepsilon_0 \varepsilon_d c_{eq}^2}{d_2 \sigma_{lv} c_2^2} V_{AB}^2.$$

Using $c_1=\varepsilon_0/d_1$ and $c_2=\varepsilon_0\varepsilon_d/d_2$ and substituting the constants $\varepsilon_0=8.854\times10^{-12}$ N m²/C², $\varepsilon_d=4.6$ (Borosilicate glass), $d_2=100$ μm, $\sigma_{lv}=0.064$ N/m (Glycerol), and $\lambda_0=605$ nm, we find $\lambda=\lambda_0+1.53\times10^{-5}V_{AB}^2$, in units of nanometers, to be independent of r.

Figure 3 shows the consecutive spectra recorded from a 6.5 μm diameter microdroplet as V_{AB} is gradually increased from 0 to 400 V. With increased V_{AB}, a redshift is clearly observed in the WGMs. In the WGM A, the maximum red shift is 3.3 nm at 400 V. This translates to an 18 nm increase in the equatorial radius, and ~7° decrease in the contact angle (assuming an unbiased contact angle of 150°). The quality factor of the WGM A also decreases with the contact angle from a resolution limited 3500 at 0 V to 2500 at 400 V. At high bias voltages, the line shape of the WGMs are observed to exhibit an asymmetry. Specifically, they develop blue shoulders. This is attributed to the nonsphericity of the microdroplet toward an oblate spheroid due to
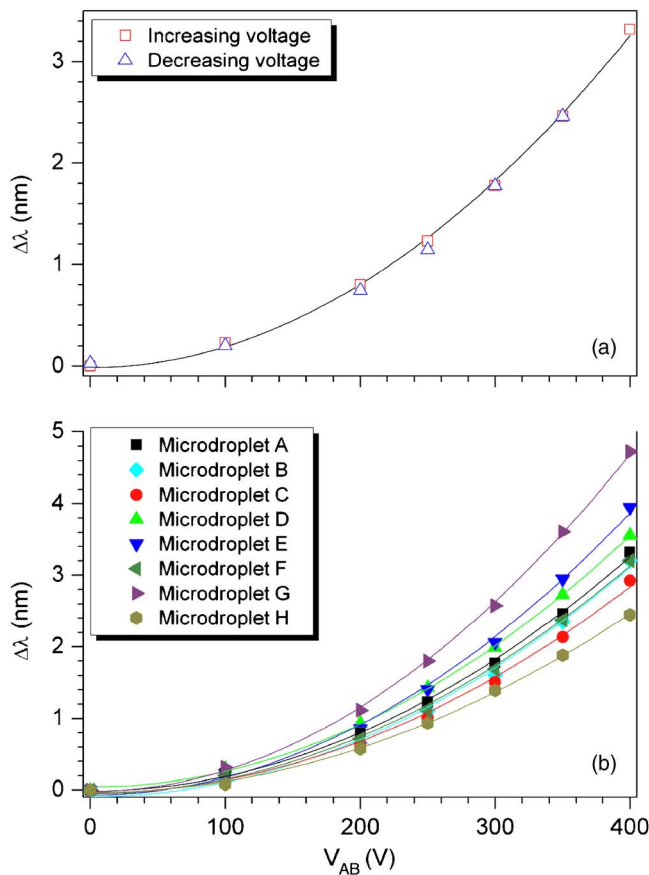
FIG. 4. (Color online) (a) Hysteresis curve of the spectral drift in the WGM A as a function of V_{AB} as V_{AB} is gradually increased from 0 to 400 V (squares) and decreased from 400 to 0 V (triangles). Solid line shows the parabolic best fit function to squares: $\Delta\lambda = 0.0145\,3 + 2.04 \times 10^{-5} V_{AB}^2$. (b) Spectral drifts of the WGMs in eight different microdroplets including the microdroplet discussed in Figs. 3 and 4(a) (microdroplet A) as a function of increasing V_{AB}. Solid lines are the parabolic best fit functions. Diameters of microdroplets B, C, D, E, F, G, and H are 5, 6, 7.5, 7, 6.5, 7, and 6 μm, respectively. A maximum spectral drift of 4.7 nm is observed at 400 V in microdroplet G.

electrowetting.[11] For an oblate spheroid, the degeneracy between the WGMs with different azimuthal mode numbers is lifted. WGMs with lower azimuthal mode numbers, that have energy densities peaked away from the equator, exhibit a blueshift compared to the WGM with highest azimuthal mode number that circulates in the equatorial plane. In our experiments, residual coupling to WGMs with lower azimuthal mode numbers is expected, even though the microdroplets are excited near their rims. We note that the non-spherical deformation only leads to the blueshifted asymmetry in the WGMs. This mechanism is different from the redshifting spectral tuning mechanism described in this letter.

The relationship between the spectral position of the WGM A in Fig. 3 and V_{AB} fits well with a parabolic function, as shown in Fig. 4(a). The slight difference between the parabolic coefficient in the best fit function (2.04×10^{-5} nm/V^2) and the theoretically predicted value (1.53×10^{-5} nm/V^2) is mainly attributed to the violation of small

changes assumption in the contact angle and deviation of the unbiased contact angle from 150°. Reversibility of the spectral tuning mechanism is also demonstrated in Fig. 4(a). As V_{AB} is decreased from 400 to 0 V, no hysteresis is observed in the spectral position of the WGM A. Figure 4(b) shows the plots of spectral drift versus V_{AB} for eight microdroplets located in the same sample chamber, including the microdroplet discussed in Figs. 3 and 4(a) (microdroplet A). Parabolic relationships are observed in all the microdroplets with parabolic coefficients ranging from 1.56×10^{-5} nm/V^2 for microdroplet H to 2.94×10^{-5} nm/V^2 for microdroplet G. At 400 V, a maximum spectral drift of 4.7 nm is observed in microdroplet G. The difference in the observed parabolic coefficients of the microdroplets can be attributed to different unbiased contact angles within an estimated range of 135°(microdroplet G)–150° (microdroplet H).

We have demonstrated a reversible electrical tuning mechanism to tune the WGMs of glycerol/water microdroplets by up to 4.7 nm at 400 V. Our results can inspire electrically tunable devices for optical communication systems based on glycerol/water microdroplets standing on a superhydrophobic surface. The use of larger diameter microdroplets can be important for future implementations, especially because of the independence of the spectral drift at a certain applied voltage from the value of the equatorial radius. In such studies, selective excitation of the high quality WGMs circulating in the equatorial plane can be achieved using fiber coupling.[12] Finally, because of the strong dependence of the parabolic coefficient to the unbiased contact angle, the presented method can be used in measuring the contact angles of microdroplets with a high accuracy.

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