Supporting Information

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Plasmonic Gas Sensing using Nanocube Patch Antennas

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The figures in this supporting information section highlight some of the properties of materials and structures used in this investigation.

Figure S1 shows the chemical structure of the Nafion Polymer used as a spacer layer. The two main components to note are the hydrophobic flouropolymer backbone and the hydrophilic sulphonic sidechain which determine its water sensitive properties.[1-3,4]

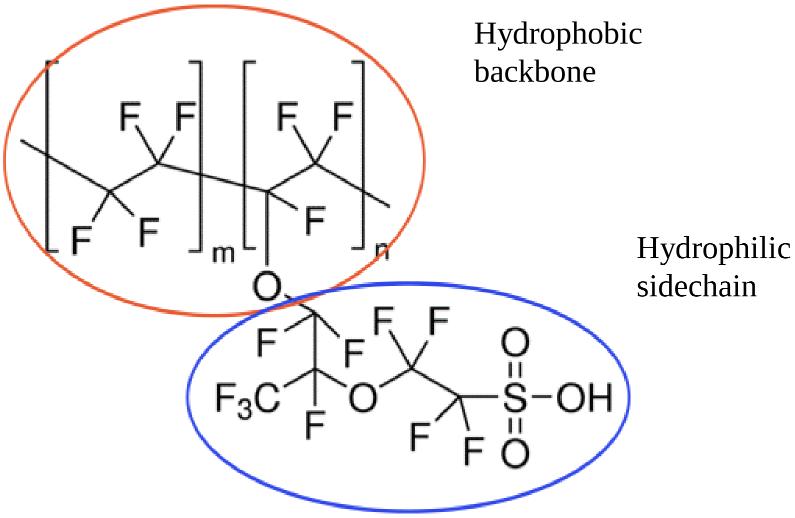

Figure S1. The structure of the Nafion fluoropolymer from Dupont, highlighting the fluoropolymer backbone and sulphonic sidechains as key elements of the structure.

Shown in **Figure S2** are the variations in NC size and RoC with a normal distribution curve fitted to each. Readings were taken through measuring TEM images of the cubes (figure S2(a)), with 70 NC's in the measured sample. The average size of the NC's is found to be 75 nm with a standard deviation of +/- 5 nm. The RoC is found to be 10 nm with a standard deviation of +/- 2 nm.

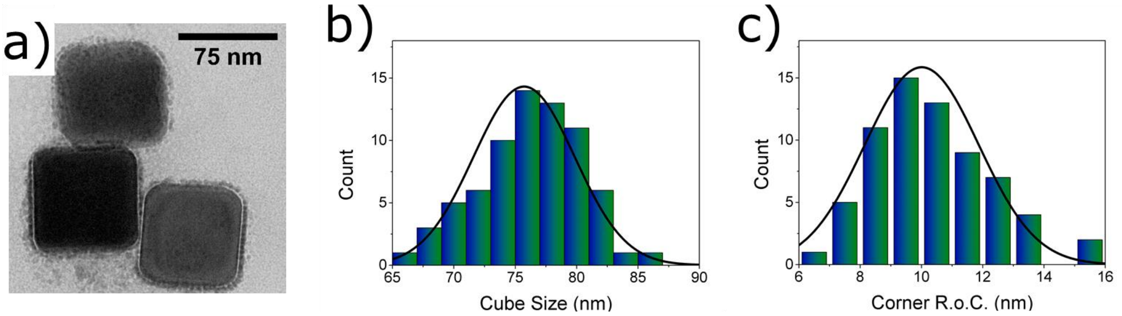

Figure S2. (a) TEM image of Ag nanocubes as received from Nanocomposix and, (b) Size and (c) corner radius of curvature measurements taken from 70 separate nanocubes using TEM images.

Effective indices of gap modes

The dispersion relation for a metal-insulator-metal waveguide can be written:[5]

$$\tanh\left(\frac{\alpha_d t}{2}\right) = -\frac{\varepsilon_m \alpha_m}{\varepsilon_d \alpha_d} \tag{S1}$$

Where: $\alpha_{m,d} = \sqrt{k_{gsp}^2 - \varepsilon_{m,d} k_o^2}$ and $k_0 = \frac{2\pi}{\lambda}$

Here k_{gsp} represents the surface plasmon-polariton (SPP) propagation constant. For small gap widths, the approximation tanh$(x)\sim x$ can be used, which produces the expression:

$$k_{gsp} \approx k_0 \sqrt{\varepsilon_d + 0.5\left(k_{gsp}^0/k_0\right)^2 + \sqrt{\left(k_{gsp}^0/k_0\right)^2\left[\varepsilon_d - \varepsilon_m + 0.25\left(k_{gsp}^0/k_0\right)^2\right]}} \tag{S2}$$

Where $\varepsilon_{d,m}$ are the spacer and metal bulk dielectric constants and $k_{gsp}{}^{0}$ represents the SPP propagation constant in the limit of very narrow gaps, $(t \to 0)$ and is described as:

$$k_{gsp}^0 = -\frac{2\varepsilon_d}{t\varepsilon_m} \tag{S3}$$

The effective index in the cavity, n_{eff} is obtained via:

$$n_{eff} = \frac{\mathrm{Re}[k_{gsp}]}{k_0} \tag{S4}$$

Bozhevolnyi *et al.* show that soltuions for equations (S1) and (S2) agree well for spacer thicknesses below ~200 nm,[5] and that this model can also be used to describe the modes inside a metal strip waveguide. This is therefore a good description of the effective index between a flat nanoparticle and the metal sheet as the optical properties of the nanorods have been shown to be very close to those of nanocubes.[6] We plot n_{eff} for Nafion spacer thicknesses of 3-40 nm using equations S2 and S3 in **Figure S3**, which shows that both curves have a similar shape but there is an offset which means that the very thin limit is only valid for films thinner than ~ 2 nm. However, it is generally expedient to consider the relationship as loosely ~*1/t* for a conceptual understanding as long as it is remembered that the actual relationship is more involved. For a more thorough theoretical treatment the reader is referred to the works of Moreau et al,[7] Cirací et al[8] and Bowen & Smith.[9]

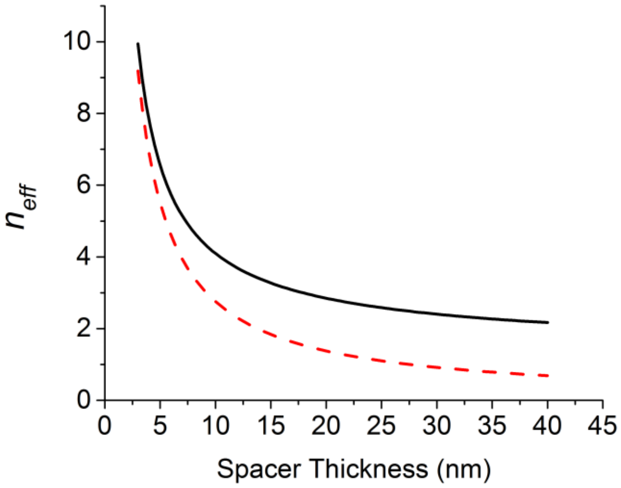

Figure S3. Plot of simulated effective index using equations 2 & 3 with an illumination wavelength of 600 nm.

Using ellipsometry to measure the RI of the Nafion films used in this investigation, a decrease in the refractive index was observed with decreasing thickness under ambient conditions, as shown in **figure S4**(a). Whilst many polymers show an increased ring-stacking for thinner spin-coated films, Nafion is a random copolymer and so the reduction in thickness actually reduces what order it had due to phase segregation, leading to poor chain stacking and increasing the free volume of the films.[10] This results in a lowering of the refractive index, a behaviour which will be key for accurately modelling the resonances of the film-coupled nanocubes throughout this report.

The refractive index decreases with expansion since the RI of water (1.33) is slightly less than that of dry Nafion (1.35), the ellipsometry results in figure S4(b) show that the RI shift is greater for thinner films, which is again due to their reduced structure allowing for greater water uptake, although as shown in figure 4, this does not have a significant impact on the resonance peaks of the nanocube antennas.

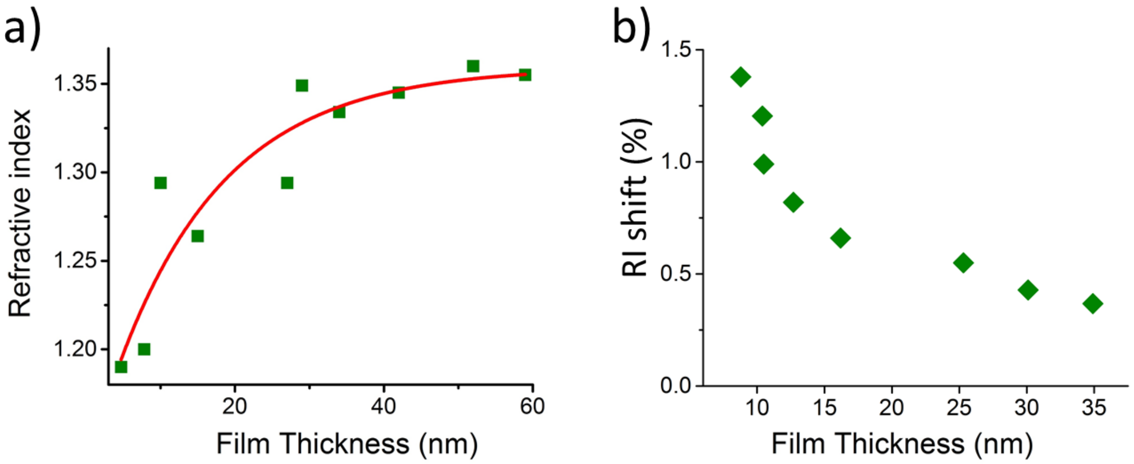

Figure S4. (a) The refractive index of thin Nafion films used in this investigation as a function of thickness, under ambient conditions as measured by ellipsometry. (b) The refractive index shift of thin Nafion films as humidity is varied from 52-85% as measured by ellipsometry.

Temperature dependence of Nafion expansion

It is worth noting that temperature has also been shown to be a factor in the RH response of Nafion, with higher temperatures leading to greater expansions. Tang et al. examined the expansion of Nafion membranes at various temperatures and found that temperature did have an effect on the swelling properties and that this was more pronounced for higher temperatures.[11] Between 25-45 ^{o}C the expansion of the membrane between 30%RH – 90%RH was found to increase from ~6.5% to ~8%, a change in swelling of 24%.

In this investigation the temperature was monitored throughout and addition of damp air was never found to alter the temperature by more than 3 ^{o}C (as shown in Fig. S5). Assuming a linear relation between temperature and swelling percentage, a difference in 3 ^{o}C would lead to a *change* in swelling of ~3.6%. (In reality the swelling % *increases* with temperature, so this assumption provides an upper limit.) For a 10 nm film with a swelling ratio of ~15% between 52-85 %RH, this results in a thickness difference of 0.05 nm, which results in a change of resonance wavelength shift of <0.5 nm compared to the case of no temperature shift. This is far smaller than the uncertainty present in Fig. 4b and so is not likely to have a significant effect on the results.

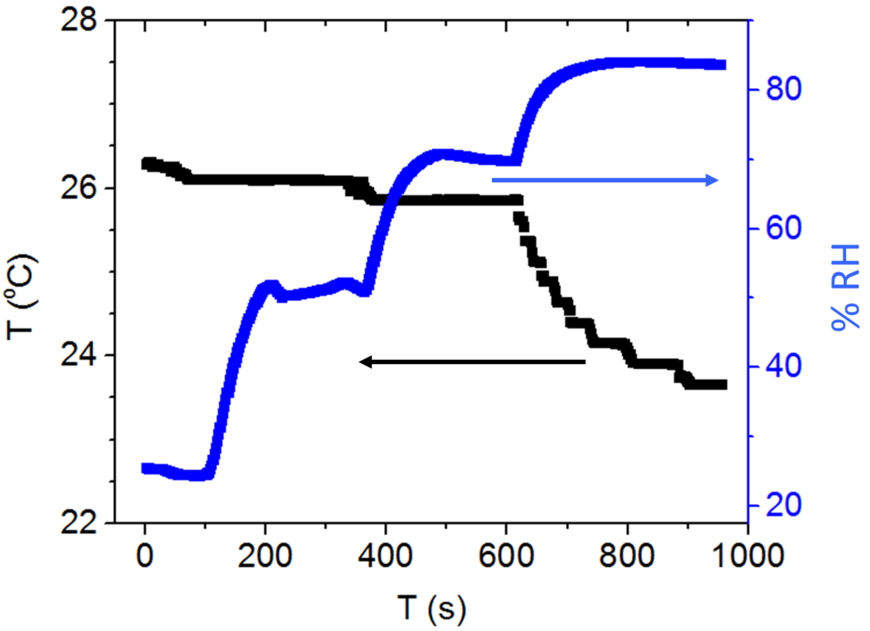

Figure S5 : Showing the change in temperature in the sample chamber as the RH is altered.

Devices designed for exterior use however would have to take temperature into account. The relation between temperature and swelling with RH as a function of ambient film thickness for very thin Nafion films would also make an interesting study. Under current experimental conditions however, the influence of temperature is not significant compared to other experimental factors.

References

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