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Statistical and Correlative Characterization of Individual Nanoparticle in Gap Plasmon Resonator Sensors

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Plasmonic nanocavities are receiing increased attention from the nanophotonics, nanoelectronics, and quantum optics community due to their ability to confine light in extremely small volumes. Coupling colloidal plasmonic nanocrystals to metal films is an inexpensive approach to fabricate virtually unlimited individual resonators that can be tuned by adjusting nanoparticle size, gap thickness, and refractive index. The focus is on silver nanocubes separated from a gold mirror by thin amorphous dielectric layers (Al_2O_3, TiO_2) . The optical response is measured and correlative electron microscopy is performed on a large number (>800) of individual resonators to unveil the statistical distribution of gap plasmon modes and assess systematically their sensitivity. A sensitivity as large as 8 nm/nm to nanocube size variation, 50 nm/nm to Al₂O₃ thickness variation, and 130 nm/RIU for index change of the spacer layer is found. With the help of numerical simulations, this approach enables to infer a quantitative statistical distribution of molecular coatings present on the nanocubes surface, such as polyvinylpyrrolidone, which can affect the performance of nanoelectronic devices and assess the strategy to remove it. Finally, polarization-resolved measurements enable to unveil a birefringent behavior when nanocubes are supported on annealed TiO_2 layers (2–4 nm).

1. Introduction

Plasmonic nanostructures have the unique ability to concentrate light into ultrasmall volumes.^[1-4] They can be created via two main approaches:^[5] top-down nanofabrication and bottom-up chemical synthesis. Top-down methods involve shaping simple

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nanoparticles and thin metal films using techniques like photolithography, soft lithography,^[6] electron-beam lithography,^[7] and nanoimprinting lithography.^[8] On the other hand, bottom-up approaches allow for largescale synthesis of plasmonic nanostructures with diverse shapes and sizes through chemical methods.^[9-11] This enables the realization of inexpensive sensing materials based on localized surface plasmon resonance,^[12-15] that is used to transduce variation of the refractive index surrounding the nanoparticles. The refractive index sensitivity (RIS) is typically defined as the ratio of the shift of the resonance wavelength $\Delta\lambda$ to the change of the refractive in-dex Δn , RIS = $\frac{\Delta\lambda}{\Delta n}$ (unit is nm/RIU, where RIU stands for refractive index unit). Elfassy et al. reported a RIS of 125 nm/RIU for silver nanocubes (Ag-NCs) of 50 nm side length^[16] whereas a sensitivity of 158 nm/RIU was observed by Martinsson et al. for 35 nm AgNCs.^[17] On the other hand, a RIS of 113 nm/RIU

for 65 nm AgNCs has been measured on quartz substrates, $^{[18]}$ 93 nm/RIU on glass and 57 nm/RIU on TiO₂, $^{[19]}$ all lower compared to that of colloidal solutions.

Most applications require resonance tunability and large field enhancement. While tuning individual particle resonances is achievable through size,^[20] thickness,^[21,22] shape,^[23,24] and material composition adjustments, coupled modes involving two or more nanoparticles have shown even greater field enhancements and improved sensitivity in sensing applications.^[25-27] However, reliable fabrication of such coupled nanoarchitectures is challenging, requiring top-down lithographic or FIB-based techniques,^[28–31] which are unsuitable for large-scale production at low cost and time consuming. Additionally, the material quality is rather poor due to the typically small crystallites obtained with such techniques, resulting in materials with large intrinsic losses.^[32,33] An alternative approach involves placing a colloidal metallic nanoparticle above a metal film with a thin dielectric spacer in between. This configuration enables to excite from the far-field a strongly confined metal-insulator-metal (MIM) mode without the need to align separate particles.^[34,35] Such architecture, known as a gap plasmon resonator, has emerged as a highly promising solution due to its unique resonance behavior and



exceptional ability to confine light in deep subwavelength volumes, generating enhanced electromagnetic fields.[34-37] Such plasmonic nanocavities have been proposed as light absorbers in thin film^[38-40] and on-chip photovoltaics,^[41,42] as platform for plasmonic sensing due to their high sensitivity to environmental changes,^[43-45] and in the development of molecular electronic devices^[46,47] as a result of the strong interaction with molecules. Among other examples, Baumberg et al. highlighted the potential of nanocavity plasmonics for chemical interrogation through surface-enhanced Raman signals, enabling localized detection and fingerprinting of molecules.[35] Hsieh et al. demonstrated ultralow threshold nanolasing in a plasmonic nanocavity, showcasing enhanced light-matter interactions for efficient lasing.^[48] In addition, Huang et al. showed tunability of emission spectra of 2D semiconductors by integrating them into plasmonic nanocavities, offering control over their optical properties.^[49] Xu et al. illustrated the enhancement of linearly polarized light emission by coupling out-of-plane excitons to anisotropic gap plasmon nanocavities, expanding the applications of these cavities to include polarization control.^[50] Additionally, Li et al. emphasized the versatility of plasmonic particle-onfilm nanocavities for enhanced spectroscopy and photochemistry applications.^[37] Gap plasmonic nanocavities have transformative potential across photocatalysis, sensing, and nanoelectronics. These structures enable tailored light-matter interactions, boosting device performance and efficiency. In photocatalysis, intensified electromagnetic fields promise more efficient catalysts. Sensing benefits from highly sensitive detection due to strong localized fields. Integrating nanocavities into nanoelectronics offers faster, energy-efficient devices. The physics of these optical cavities has been extensively studied theoretically and experimentally,^[20,35,51,52] and the impact of various parameters such as geometry, gap size, morphology,^[53,54] composition and surrounding dielectric medium^[55] has been explored.^[56-58]

However, the sensitivity of gap plasmon resonators to refractive index changes of the gap spacer is currently underexplored. In addition, accurate statistical measurements of the sensitivity of such nanocavity systems are currently unavailable due to the resonance broadening (>100 nm) observed during spectroscopy of an ensemble of resonators, resulting in spectra that are difficult to compare to numerical predictions (the typical full width half maximum of individual resonators being below 30 nm). Moreover, the intrinsic variability of individual resonators having identical geometrical parameters is still undetermined. Therefore, extensive characterization of individual resonators, combined with correlative electron microscopy are needed to fill these gaps.

Here, we rigorously explore how individual resonators are affected by subtle changes of their environment, by analyzing gap plasmon resonances (GPR) of silver nanocubes separated from a gold film by ultra-thin dielectric layers. These modes are probed in the far-field using an inverted microscope coupled to an optical fiber that spatially select scattered light from a diffraction-limited area prior to spectral analysis. First, we characterized the sensitivity to various atomic layer deposition (ALD)-grown dielectric layers, Al₂O₃ and TiO₂,^[59,60] with different thicknesses and nanocube sizes, supported by correlative scanning electron microscopy (SEM) and numerical simulations. We confirmed a linear relationship between nanocube size and resonance wave-

length, as predicted by the Fabry–Perot model.^[61,62] Larger sensitivity is obtained for thinner dielectric layers, as confirmed by numerical simulations. Measurements on a large number of individual resonators (>800) revealed a statistically significant variability despite identical nominal conditions. Coupling with transmission electron microscopy (TEM) analysis and numerical simulations we concluded that the intrinsic variability of polyvinylpirrolidone (PVP) adsorbed on the nanoparticles is responsible for the fluctuations observed. Using individual resonators as thickness^[63] rulers enabled us to infer the statistical distribution of the PVP coating with an Ångström resolution. In addition, this also led us to refine the PVP removal process prior to nanocube deposition, which is crucial for effective implementation in nanoelectronics.

Finally, we explored the opportunity to use this platform to study the impact of annealing on ultrathin TiO₂ layers by means of polarization-resolved measurements. In addition to a prevalent use in fields such as photovoltaics, photocatalysis, and sensing, [64-66] TiO₂ can be crystallized by annealing at relatively low temperature. We observed the fundamental mode splitting into two resonances that can be selected by linear polarization of the incident beam. We hypothesize that this unexpected behavior could result from some anisotropy induced in the spacer layer by annealing. In fact, in the anatase or rutile phase TiO₂ exhibits birefringence,[67,68] therefore it possesses different refractive indices along different crystal axes. A distribution of grain orientation underneath the nanocubes can lead to a polarizationdependent spectrum. Full control and understanding of this behavior can be useful for designing tailored plasmonic devices with enhanced functionalities, but also as a mean to characterize crystalline layers via optical methods with resolution below the diffraction limit. Plasmonic sensing, photovoltaics, photocatalysis, nanoelectronics and other optical related applications can benefit from this study.

2. Results and Discussion

The plasmonic nanocavities consisted of a collection of silver nanocubes (AgNCs) on a gold film separated by a dielectric layer (thickness "g"), as illustrated in Figure 1a. This design enables extreme light confinement and precise control of the mode volume, that is achieved by tuning the thickness of the dielectric spacer with sub-nanometer precision via ALD.^[69] The AgNCs, synthesized via the polyol process,^[70] have an average size of 50–60 nm, are uniform in shape (Figure S1, Supporting Information) and are coated with a thin layer of PVP used as shape-directing agent. When excited in dark field (DF), individual nanocube resonators exhibited distinct red doughnut-like shapes^[52] indicating a strong interaction between the nanocubes and the metal film (Figure 1b). As the spacer thickness exceeded 10 nm, the interaction weakened, as evidenced by a continuous blueshift, whereas the radiation profile transitioned from the doughnut shape to a solid dot (Figure S2, Supporting Information). This transition has been linked to a change in orientation of the dominant radiation dipole from vertical (narrow gaps) to in-plane (wide gaps), as a consequence to a change in coupling efficiency to the different modes.

We examined the features of the plasmonic nanocavity system by exciting individual nanocubes in bright-field via a ADVANCED SCIENCE NEWS ______



Figure 1. a) Scheme of the plasmonic nanocavity system, b) dark field optical image of silver NCoM, c) SEM image of an individual silver nanocube, and d) representative bright reflectance spectrum of an individual NCoM resonator, normalized by the gold film. The dependence of gap plasmon resonance on e) nanocube size and gap thickness. f) A contour plot was generated using the experimental results, illustrating the average spectra of the gap plasmon resonance for AgNCs on Al_2O_3/Au with varying e) nanocube size and f) gap thickness. Absorption efficiency of AgNCs on Al_2O_3/Au as a function of g) nanocube size and h) Al_2O_3 thickness, obtained via BEM simulations.

micro-spectroscopy setup with a diffraction-limited spatial resolution. The investigation of individual nanocube-on-mirror (NCoM) structure resulted in consistent resonance peaks. Figure 1d shows a typical spectrum of an individual resonator, taking as reference the gold film in a location without nanocubes. Light is absorbed and scattered as a result of coupling to gap plasmon modes. The presence of several peaks indicates the existence of different hybridized modes.^[53] Note that the full width half maximum of the low energy mode is $\approx 25-30$ nm, corresponding to a quality factor (Q) near 30. This a characteristic of an individual nanocube resonators, in contrast with that observed in ensemble measurements (Q ≈ 6 , see Figure S3, Supporting Information).

The size and morphology of individual nanocubes were characterized by SEM to allow for correlation with their respective spectra. This enabled us to determine how GPR evolves as a function of the geometric parameters of the nanocubes and to compare with numerical simulations. Figure 1 shows the impact of nanocube size (at constant Al₂O₃ thickness, Figure 1e) and that of Al₂O₃ thickness (at constant nanocube size, Figure 1f). Spectra were obtained from roughly 100 individual nanocubes for each thickness (see Figures S4 and S5, Supporting Information, for detailed spectra). Figure 1g,h illustrates the respective absorption efficiency simulated at 65° excitation, corresponding to the maximum numerical aperture used to collect the spectra. The measurements indicate that, as the edge length of the nanocube increases, the GPR undergoes a redshift, due to the increase in cavity width, in close agreement to the simulations presented in Figure 1g. The linear trend of the resonance wavelength with the edge length can also be predicted using a simplified FabryPerot model,^[61,62] and is indicative of a cavity mode.^[71] Additionally, absorption efficiency increases by roughly 50% when the nanocube size increases from 45 to 60 nm. The resulting sensitivity of the fundamental mode to nanocube size variation ($\Delta\lambda/\Delta L$) is 8 nm/nm.

In Figure 1f, the gap thickness was varied from 0.5 to 4 nm (0.5, 1, 2, 3, and 4 nm), while maintaining a fixed nanocube size of 60 nm. This led to a redshift for thinner amorphous Al₂O₃ layers, which agrees with the simulations presented in Figure 1h. This is consistent with literature^[72,73] and is attributed to an increase of the effective mode index as the coupling between the nanocube and the metal film intensifies. This could also be viewed as a weakening (strengthening) of the Coulomb interaction between the surface charge on the nanocube and its mirror image when the distance between them becomes larger (smaller), directly impacting the energy of the resonator. The resulting sensitivity of the fundamental mode to Al₂O₃ thickness variation ($\Delta\lambda/\Delta g$) is 50 nm/nm.

These experimental results confirm that individual gap plasmon resonators are effective light absorbers. Most measurements reveal an apparent extinction of 5–9%, which is roughly five times larger than the corresponding absorption cross-section. This overestimation of the absorptance is attributed to the limited numerical aperture of the objective, which results in uncollected light scattered at large angles. The enhanced coupling between the nanocube and the mirror in thinner Al_2O_3 layers is evidenced by the resonance redshift. This is further illustrated in **Figure 2a**,b, which presents the influence of the nanocube size on the low energy mode with varying Al_2O_3 thicknesses. Although the sensitivity to a change in nanocube size

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Figure 2. Data plot of gap plasmon resonance for different Al_2O_3 spacer thicknesses. a) Linear regression of individual resonators (solid line) with 90% confidence interval (dashed line) as a function of nanocube size for various Al_2O_3 thicknesses. b) Contour plot of gap plasmon resonance position with wavelength as a function of nanocube size and Al_2O_3 thickness. c) Histogram of the center gap plasmon resonance wavelength statistical distribution for 50 and 60 nm nanocubes.

(slope of the curves) is expected to become larger for thinner layers as a result of the stronger coupling, we do not observe an obvious trend in the slopes. This can be attributed to the presence of the (≈4 nm) polyvinylpyrrolidone (PVP) capping layer residual from the nanocube synthesis (see next), resulting in a substantial increase of the overall thickness. As a consequence, the difference in sensitivity among different Al₂O₃ layers is small, as illustrated in Figure S6 (Supporting Information) and lies within the noise of the measurements. The map shown in Figure 2b summarizes the experimental results, highlighting the impact that dielectric thickness and nanocube size have on the resonance wavelength.^[74,75] These results indicate that the spectral response of the resonators can be tuned in a wide range of wavelength by changing nanocube size and gap spacer thickness. In Figure 2c we show the histograms of gap plasmon center wavelength for many individual NCoMs with a size of 50 and 60 nm, supported on dielectric layers of various thicknesses. These histograms unveil a statistical distribution of resonance wavelengths across many individual nanoparticles of nearly the same size, regardless of Al₂O₃ thickness. This was unexpected since resonators with identical geometrical parameters should yield a mono-modal distribution of center wavelengths.

As mentioned earlier, the nanocubes are coated with a thin layer of PVP, used as shape-directing agent in the synthesis. We hypothesized that the stochastic thickness distribution of this layer was responsible for the resonance variability. TEM analysis showed that the PVP thickness varies across different nanocubes (Figures S7 and S8, Supporting Information), corroborating our hypothesis. Such residual PVP layer acts as an insulator, results in high contact resistance and hinders the efficacy of AgNCs in electronic applications, sensing, catalysis, and surface-enhanced Raman spectroscopy (SERS).^[76,77] Therefore, there is a strong drive to precisely quantify its thickness. In **Figure 3** we show that correlative characterization of individual NCoMs can serve as an effective optical sensor to i) infer the thickness distribution of such molecular layers with Ångström resolution, and ii) to evaluate the effectiveness of procedures for PVP removal.

The effect of the PVP thickness on the GPR was investigated by numerical simulations. Figure 3a shows the absorption crosssection of a gap plasmon resonator as a function of PVP thickness at 65° excitation, for 60 nm nanocubes on 2 nm Al_2O_3 . Several modes can be observed. The modes shift toward the red as the PVP thickness decreases, as expected. If the PVP thickness increases, the modes linewidth widens as they approach each other.

Sodium borohydride (NaBH₄) was used to remove PVP (see Supporting Information for further details), as confirmed by TEM (Figure 3d–g). Fifty spectra were measured on 60 nm Ag-NCs before and after PVP removal, and these plots were averaged to create a single representative spectrum (Figure 3b). The GPR shifted from \approx 650 to \approx 730 nm after exposure to NaBH₄, corresponding to a thickness decrease of PVP from \approx 4 to <2 nm, calculated from simulations (Figure 3a). There is a substantial variability of GPR, as indicated by the standard deviation of experimental data. To highlight such variability, we present the data by showing the histogram of center wavelengths in Figure 3c (left) and use simulation of the fundamental mode (center) to infer a PVP thickness histogram (bottom) across many individual NCoMs, showing substantial variability, both before and after removal.

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Figure 3. Quantification of PVP thickness using plasmonic nanocavity system. a) Absorption cross-section as a function of PVP thickness under 65° on Al₂O₃/Au. b) Averaged spectra before and after removal of PVP. Shadow areas represent standard deviations calculated for each point. Dots indicate the average gap plasmon resonance values obtained by fitting each spectrum with a Lorentzian function, and the corresponding standard deviations. c) Fundamental mode wavelength (black square) compared with the experimental results from average gap plasmon resonance position on nanocubes before and after removal of PVP (red square). Dots and bars are the mean values and standard deviations. The inset shows the histograms of gap plasmon center wavelength across many individual resonators. TEM images of the individual nanocube d,e) before removing PVP and f,g) after removing PVP.

Statistical TEM analysis revealed that before removal, the PVP thickness is $\approx 4.0 \pm 3.4$ nm (Figures S7 and S8, Supporting Information), and decreases to 1.5 ± 0.9 nm after exposure to NaBH₄, in good agreement with simulations. These results highlight the usefulness of this approach for precise optical measurements of sub-nanometer material thicknesses and provide with a quick methodology to access the statistical distribution of molecular coatings for further understanding their impact on various applications.

Next, we experimentally evaluated the sensitivity of the GPR to changes in the refractive index of the gap spacer layer. Different dielectric materials, Al_2O_3 and TiO_2 , were studied. The refractive indices, measured via ellipsometry, are reported in

Figure S9a,b (Supporting Information), and are 1.615 and 2.427 at a wavelength of 0.520 μ m, respectively. GPR measurements were conducted on \approx 80 individual nanocubes (50–60 nm) per sample, for different dielectric thicknesses, as reported in Figure 4a–c. As expected, a redshift is observed when the refractive index of the dielectric increases, with an average shift of \approx 60 nm \pm 25 nm for a 2 nm gap, 100 nm \pm 17 nm for a 3 nm gap, and 83 nm \pm 30 nm for a 4 nm gap with 60 nm AgNCs.

Considering that the interactions between the nanocube and the adjacent metal film strongly influence the resonant properties of the system and its local electromagnetic field distribution, we expect a substantial impact on the sensitivity. We determined the sensitivity for different thicknesses of Al_2O_3 and TiO_2 , as SCIENCE NEWS ____

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Figure 4. The sensitivity of gap plasmon resonance. a–c) Histogram of the center gap plasmon resonance wavelength of 60 ± 2 nm AgNCs on difference spacer Al₂O₃ and TiO₂ thicknesses and the experimental results of gap plasmon resonance of individual AgNCs on Al₂O₃/Au films with gap refractive index changes from Al₂O₃ to TiO₂ and gap thickness change from 2, 3, to 4 nm. (d) The average sensitivity of AgNCs on Au films with gap refractive index changes from Al₂O₃ to TiO₂. e) Comparison of average sensitivity between 50 and 60 nm AgNCs as a function of gap thickness.

summarized in Figure 4d. These results indicate that the average sensitivity on 50 nm AgNCs is higher than that on 60 nm AgNCs across all dielectric thicknesses. Smaller nanocubes tend to exhibit more pronounced plasmonic effects due to their relatively larger surface-to-volume ratio.^[78] This increased plasmonic activity makes them more responsive to changes in the local elec-

tromagnetic environment, such as those caused by variations in the refractive index of the gap spacer layer. It is worth noticing that other factors, such as the thickness of the PVP layer capping the nanocubes may influence sensitivity. In this study, the PVP thickness was observed to be larger in the case of the 60 nm AgNCs compared to the 50 nm AgNCs. This can contribute to

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the different sensitivity observed. In addition, larger sensitivity is obtained for 3 nm gaps, regardless of nanocube size.^[70] Note that this sensitivity refers to refractive index changes of the spacer layer and cannot be directly compared to changes of the dielectric surrounding the nanocubes, that is instead the typical figure of merit of nanoparticle-based sensors. Nevertheless, Figure 4 shows that a RIS of 130 nm/RIU is remarkable, given that the index change takes place in a minute volume (the spacer layer). For comparison, nanocubes immobilized on TiO₂ displayed a sensitivity of 57 nm/RIU only, despite the change of the entire dielectric surrounding the nanocube.^[19]

Literature on GPR revolves around amorphous inorganic layers or molecular layers, so there is an interest in exploring how it is affected by the presence of a crystalline spacer layer. To this mean, the TiO₂ layer was annealed to promote crystallization. TiO₂ has three main crystalline phases: anatase, rutile, and brookite. Among these phases, anatase is a metastable phase commonly obtained by annealing TiO₂ thin films at temperatures in the 300–500 °C range.^[79,80] We characterized individual plasmonic nanocavities on annealed ultrathin TiO₂ layers. The annealing procedure employed enables to fully crystallize ALD-grown TiO₂ layers into anatase, as evidenced by XRD (Figure S10, Supporting Information) and Raman (Figure S11, Supporting Information) measurements on films with thickness in the range of 10–50 nm.

Figure 5 compares polarization-resolved measurements on 4 nm TiO₂ films before and after annealing. The spectrum obtained on amorphous TiO₂ shows a single peak at \approx 700 nm, which is consistent with the GPR behavior discussed in the previous section. After annealing, two peaks are observed in the spectrum when incident light is unpolarized. To further characterize the plasmonic response we performed polarization-resolved measurements by inserting a linear polarizer in the excitation pathway. The resulting spectra showed in most cases only one of the two peaks, or a substantial change in their relative intensity compared to unpolarized measurements. Rotating the polarizer by 90° resulted in the suppression of the other peak. The magnitude of the splitting varied across the individual nanocubes measured. Additionally, for a given linear polarization, the suppression of the low-energy peak or the high-energy peak could be observed. Two representative spectra of individual nanocubes supported on annealed 4 nm TiO₂ films are reported in Figure 5b,c. Conversely, polarization-resolved measurements on TiO₂ before annealing did not show significant differences. The peak splitting $(\Delta \lambda)$ across 28 individual nanocubes is reported in Figure 5d–f for different dielectric thicknesses. The data have been ordered from low to high $\Delta \lambda$. In Figure 5g–i we show the peak selection as a function of polarization, calculated as a function of the area of the peak normalized by the total area of the spectrum. In red, we show the results for the low-energy mode and, in blue, for the high-energy mode, with 100% meaning perfect selection. Switching the polarization leads to a switch of the peak suppressed. These results indicate that a large variability is observed in terms of the magnitude of peak shift and suppression, but also with regards to which of the two peaks is mostly suppressed for a given linear polarization. Correlative SEM characterization confirmed the cubic shape of the nanoparticle analyzed, therefore ruling out asymmetries as a possible cause for the observed behavior. The roughness of the TiO₂ surfaces on both amorphous and annealed substrates was comparable, as shown in Figure S12 (Supporting Information). This allows to exclude tilting of nanocubes on annealed surfaces as a source for the observed asymmetric response to polarized light. We hypothesized that the birefringence of annealed TiO_2 could explain the experimental results. Electron backscatter diffraction (EBSD) was used to characterize the crystallographic orientation of the supporting gold film. In EBSD an electron beam is directed onto the surface of the sample, resulting in back-scattered electrons that form a Kikuchi pattern correlating with the structure and orientation of the crystal lattice. Analysis showed that the gold film (after deposit and thermal treatment) is polycrystalline, and the surfaces of the grains are mostly oriented with their (111) plane is parallel to the substrate (Figures S13 and S14, Supporting Information).

EBSD was also performed on 50 nm thick TiO₂ supported on the Au substrate after annealing at 350 °C for 2 h to determine the presence of epitaxy. It was found that TiO₂ anatase crystals prefer to align with their (011) plane on the Au substrate, as a result of the fact that the (011) plane is the most stable, having a lower surface energy compared to the other planes.^[81] While other grain orientations were observed, the preferred orientation is close to (011) facet (S15 and S16), but no in-plane epitaxy was found between the Au substrate and TiO₂ crystals.

FDTD simulations were performed to unravel any correlation between the crystal orientation of the birefringent TiO₂ layer and the GPR. The dielectric layer was modeled with a constant refractive index (n) of 2.5 at 0.520 μ m and a birefringence of ± 0.1 . To simulate all possible orientation of the crystal, several simulations were performed changing the axis with birefringence. These simulations evidenced that the GPR is mostly depending on the value of n_{x} , whereas the value of n_{y} and n_{y} have almost negligible impact, as shown in Figure S17 (Supporting Information). Therefore, it appears that in homogeneous layers birefringence does not play a significant role, since n_{τ} is orthogonal to the polarization axes. A possible explanation for our experimental results is that TiO₂ grains are smaller than the nanocube size, which could be expected given the absence of epitaxy with the underlying Au substrate and confirmed by XRD and EBSD. As a result, each nanocube is deposited on various grains with a distribution of crystallographic orientations and possibly different allotrope phases, and therefore of n_{r} . The GPR has two maxima at the nanocube edges and a node in the center. Therefore, if adjacent edges of a nanocube are on grains of different orientation (or refractive index) we expect a polarization dependence of the spectrum, as evidenced by numerical simulations shown in Figure S18 (Supporting Information). Further work is needed to confirm this hypothesis explaining the behavior of gap-plasmon modes in annealed TiO₂ films. This could pave the way for optical crystallography of ultrathin films below the diffraction limit.

3. Conclusion

In summary, our theoretical and correlative experimental analyses on individual nanocubes have highlighted the significant influence of nanoparticle size, gap spacer thickness, and refractive index on the coupling between plasmonic components in a plasmonic nanocavity system. Gap thickness and nanocube size can be used to tune the spectral response in a wide range of wavelength, and to increase sensitivity to the refractive index of the www.advancedsciencenews.com

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Figure 5. The gap plasmonic resonance spectrum of individual AgNC on TiO₂ depending on a spacer layer with different polarizations. a) Reflectance spectra on TiO₂ amorphous as a spacer layer. b,c) Reflectance spectra on annealed TiO₂ with different polarizations. The peak splitting ($\Delta\lambda$) d) 2, e) 3, and f) 4 nm TiO₂ and peak selection as a function of polarization across different individual nanocubes g) 2, h) 3, and i) 4 nm TiO₂.

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spacer layer, making it a promising option for optical sensing. As an example, we showed the characterization of the residual PVP capping layer around nanocubes, which is critical for the integration in nanoelectronics systems. Finally, polarization-resolved measurements on annealed TiO_2 layers evidenced a birefringence in the system response, possibly due to a distribution of grain orientation in the birefringent polycrystalline spacer. If confirmed, this could be a unique and powerful way to gain insight into the crystallographic orientation of anisotropic material at a nanometer scale. This shows the interest in studying the behavior of GPR in complex systems, such as anisotropic materials. The integration of the techniques mentioned above provided us with a comprehensive understanding of the properties and behavior of the plasmonic nanocavity system, highlighting the need for correlative characterization of individual nanoparticles.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

crystalline structure, gap plasmon resonators, individual nanoparticles, nanocubes, plasmonic cavities, plasmonic rulers, sensor

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- [1] G. Barbillon, Materials 2019, 12, 1502.
- [2] S. Marquez, E. Morales-Narváez, Front. Bioeng. Biotechnol. 2019, 7, 69.
- [3] S. A. Maier, in *Plasmonics: Fundamentals and Applications*, Springer, New York, 2007, p. 3-220.
- [4] T. V. Shahbazyan, M. I. Stockman, in *Plasmonics: Theory and Applica*tions, Dordrecht, Springer Netherlands, 2013.

- [5] G. Lérondel, S. Kostcheev, J. Plain, In *Plasmonics: From Basics to Advanced Topics*, (Eds: S. Enoch, N. Bonod), Springer, Berlin Heidelberg 2012, pp. 269-316.
- [6] Y. Xia, G. M. Whitesides, S. Lithography, Angew. Chem., Int. Ed. 1998, 37, 550.
- [7] M. Horák, K. Bukvišová, V. Švarc, J. Jaskowiec, V. Křápek, T. Šikola, *Sci. Rep.* 2018, 8, 9640.
- [8] S. Y. Chou, P. R. Krauss, P. J. Renstrom, J. Vacuum Sci. Technol. B 1996, 14, 4129.
- [9] F. Yao, F. Li, Z. He, Y. Liu, L. Xu, X. Han, Appl. Sci. 2020, 10, 2603.
- [10] L. Malassis, P. Massé, M. Tréguer-Delapierre, S. Mornet, P. Weisbecker, V. Kravets, A. Grigorenko, P. Barois, *Langmuir* 2013, 29, 1551.
- [11] A. Capitaine, B. Sciacca, Adv. Mater. 2022, 34, 2200364.
- [12] A. Bonyár, Biosensors 2021, 11, 527.
- [13] M. H. Tu, T. Sun, K. T. V. Grattan, Sens. Actuators B: Chem. 2014, 191, 37.
- [14] A. A. Yanik, M. Huang, A. Artar, T.-Y. Chang, H. Altug, On-Chip Nanoplasmonic Biosensors with Actively Controlled Nanofluidic Surface Delivery, SPIE, Bellingham, WA 2010.
- [15] M. Piliarik, P. Kvasnička, N. Galler, J. R. Krenn, J. Homola, *Opt. Express* 2011, *19*, 9213.
- [16] E. Elfassy, Y. Mastai, A. Salomon, J. Solid State Chem. 2016, 241, 110.
- [17] E. Martinsson, M. A. Otte, M. M. Shahjamali, B. Sepulveda, D. Aili, J. Phys. Chem. C 2014, 118, 24680.
- [18] M. A. Mahmoud, M. Chamanzar, A. Adibi, M. A. El-Sayed, J. Am. Chem. Soc. 2012, 134, 6434.
- [19] N. Ahamad, A. Bottomley, A. Ianoul, J. Phys. Chem. C 2012, 116, 185.
- [20] A. Li, S. Isaacs, I. Abdulhalim, S. Li, J. Phys. Chem. C 2015, 119, 19382.
- [21] P. Sadeghi, K. Wu, T. Rindzevicius, A. Boisen, S. Schmid, Nanophotonics 2018, 7, 479.
- [22] V. Devaraj, J.-M. Lee, J.-W. Oh, Nanomaterials 2018, 8, 582.
- [23] J. J. Mock, R. T. Hill, A. Degiron, S. Zauscher, A. Chilkoti, D. R. Smith, *Nano Lett.* 2008, 8, 2245.
- [24] X. Huang, B. Zhang, B. Yu, H. Zhang, G. Shao, Nanotechnology 2022, 33, 225206.
- [25] K. M. Mayer, J. H. Hafner, Chem. Rev. 2011, 111, 3828.
- [26] S. M. Kim, H. J. Kim, H. J. Jung, J.-Y. Park, T. J. Seok, Y.-H. Choa, T. J. Park, S. W. Lee, *Adv. Funct. Mater.* **2019**, *29*, 1970039.
- [27] S.-Y. Ding, E.-M. You, Z.-Q. Tian, M. Moskovits, Chem. Soc. Rev. 2017, 46, 4042.
- [28] Q. Y. Lin, J. A. Mason, Z. Li, W. Zhou, M. N. O'Brien, K. A. Brown, M. R. Jones, S. Butun, B. Lee, V. P. Dravid, K. Aydin, C. A. Mirkin, *Science* **2018**, *359*, 669.
- [29] H.-R. Park, X. Chen, N.-C. Nguyen, J. Peraire, S.-H. Oh, ACS Photonics 2015, 2, 417.
- [30] S. Kasani, K. Curtin, N. Wu, Nanophotonics 2019, 8, 2065.
- [31] I. Bouanane, F. Bedu, I. Ozerov, B. Sciacca, L. Santinacci, D. Duché, G. Berginc, L. Escoubas, O. Margeat, J. Le Rouzo, *Sci. Rep.* 2023, 13, 7770.
- [32] Y. Wu, C. Zhang, N. M. Estakhri, Y. Zhao, J. Kim, M. Zhang, X.-X. Liu, G. K. Pribil, A. Alù, C.-K. Shih, X. Li, *Adv. Mater.* **2014**, *26*, 6106.
- [33] Z. Lao, Y. Zheng, Y. Dai, Y. Hu, J. Ni, S. Ji, Z. Cai, Z. J. Smith, J. Li, L. Zhang, D. Wu, J. Chu, Adv. Funct. Mater. 2020, 30, 1909467.
- [34] H. Sugimoto, M. Fujii, ACS Photonics 2018, 5, 1986.
- [35] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, D. R. Smith, Nat. Mater. 2019, 18, 668.
- [36] V. Devaraj, H. Jeong, C. Kim, J.-M. Lee, J.-W. Oh, *Coatings* 2019, 9, 387.
- [37] G.-C. Li, Q. Zhang, S. A. Maier, D. Lei, Nanophotonics 2018, 7, 1865.
- [38] M. M. Tharwat, A. Almalki, A. M. Mahros, *Materials* 2021, 14, 1380.
- [39] R. A. Pala, J. White, E. Barnard, J. Liu, M. L. Brongersma, Adv. Mater. 2009, 21, 3504.

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- [40] R. Siavash Moakhar, S. Gholipour, S. Masudy-Panah, A. Seza, A. Mehdikhani, N. Riahi-Noori, S. Tafazoli, N. Timasi, Y.-F. Lim, M. Saliba, *Adv. Sci.* 2020, *7*, 1902448.
- [41] M. Stockman, K. Kneipp, S. Bozhevolnyi, S. Saha, A. Dutta, J. Ndukaife, N. Kinsey, H. Reddy, U. Guler, V. Shalaev, A. Boltasseva, B. Gholipour, H. Swaha Krishnamoorthy, K. MacDonald, C. Soci, N. Zheludev, V. Savinov, R. Singh, P. Gross, M. Kling, J. Opt. 2017, 20, 043001.
- [42] L. Feng, M. Niu, Z. Wen, X. Hao, Polymers 2018, 10, 123.
- [43] M. Li, S. K. Cushing, N. Wu, Analyst 2015, 140, 386.
- [44] A. A. Rifat, R. Ahmed, A. K. Yetisen, H. Butt, A. Sabouri, G. A. Mahdiraji, S. H. Yun, F. R. M. Adikan, *Sens. Actuators, B* **2017**, *243*, 311.
- [45] R. Taylor, F. Benz, D. Sigle, R. Bowman, P. Bao, J. Roth, G. Heath, S. Evans, J. Baumberg, *Scientific Rep.* 2014, 4, 5940.
- [46] Q.-Y. Lin, Z. Li, K. A. Brown, M. N. O'Brien, M. B. Ross, Y. Zhou, S. Butun, P.-C. Chen, G. C. Schatz, V. P. Dravid, K. Aydin, C. A. Mirkin, *Nano Lett.* **2015**, *15*, 4699.
- [47] T. Wang, C. A. Nijhuis, Appl. Mater. Today 2016, 3, 73.
- [48] Y. K. Hsieh, B.-W. Hsu, K.-N. Peng, K.-W. Lee, C. W. Chu, S. W. Chang, H. W. Lin, T. J. Yen, Y. Lu, ACS Nano 2020, 14, 11670.
- [49] J. Huang, G. M. Akselrod, M. Tian, J. Kong, M. H. Mikkelsen, ACS Photonics 2017, 5, 552.
- [50] K. Xu, Z. Zou, W. Li, L. Zhang, M. Ge, T. Wang, W. Du, Nano Lett. 2024, 24, 3647.
- [51] V. Devaraj, J.-M. Lee, J.-W. Oh, Curr. Appl. Phys. 2020, 20, 1335.
- [52] R. Chikkaraddy, X. Zheng, F. Benz, L. J. Brooks, B. de Nijs, C. Carnegie, M.-E. Kleemann, J. Mertens, R. W. Bowman, G. A. E. Vandenbosch, V. V. Moshchalkov, J. J. Baumberg, ACS Photonics 2017, 4, 469.
- [53] J. Zhang, X. Zhang, Adv. Mater. Interfaces 2018, 5, 1800580.
- [54] J. Ye, P. V. Dorpe, Nanoscale 2012, 4, 7205.
- [55] A. Bonyár, I. Csarnovics, G. Szántó, Photonics and Nanostructures Fundamentals and Applications, Elsevier, New York 2018, Vol. 31, p. 1.
- [56] S. Boroviks, Z.-H. Lin, V. A. Zenin, M. Ziegler, A. Dellith, P. A. D. Gonçalves, C. Wolff, S. I. Bozhevolnyi, J.-S. Huang, N. A. Mortensen, *Nat. Commun.* 2022, 13, 3105.
- [57] V. Devaraj, I. H. Lee, M. Kim, T. M. Nguyen, J. P. Son, J.-M. Lee, D. Lee, K. H. Kim, J.-W. Oh, Curr. Appl. Phys. 2022, 44, 22.
- [58] A. Capitaine, M. Bochet-Modaresialam, P. Poungsripong, C. Badie, V. Heresanu, O. Margeat, L. Santinacci, D. Grosso, E. Garnett, B. Sciacca, ACS Nano 2023, 17, 9361.
- [59] P. Roy, C. Badie, J.-B. Claude, A. Barulin, A. Moreau, J. Lumeau, M. Abbarchi, L. Santinacci, J. Wenger, ACS Appl. Nano Mater. 2021, 4, 7199.

- [60] M. E. Dufond, M. W. Diouf, C. Badie, C. Laffon, P. Parent, D. Ferry, D. Grosso, J. C. S. Kools, S. D. Elliott, L. Santinacci, *Chem. Mater.* 2020, 32, 1393.
- [61] H.-J. Li, L.-L. Wang, B. Sun, Z.-R. Huang, X. Zhai, Plasmonics 2015, 11, 87.
- [62] H. Ditlbacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F. R. Aussenegg, J. R. Krenn, Phys. Rev. Lett. 2005, 95, 257403.
- [63] R. T. Hill, J. J. Mock, A. Hucknall, S. D. Wolter, N. M. Jokerst, D. R. Smith, A. Chilkoti, ACS Nano 2012, 6, 9237.
- [64] X. Kang, S. Liu, Z. Dai, Y. He, X. Song, Z. Tan, Catalysts 2019, 9, 191.
- [65] R. L. Wilson, C. E. Simion, C. S. Blackman, C. J. Carmalt, A. Stanoiu, F. Di Maggio, J. A. Covington, Sensors 2018, 18, 735.
- [66] A. K. Chandiran, A. Yella, M. Stefik, L.-P. Heiniger, P. Comte, M. Nazeeruddin, M. Graetzel, ACS Appl. Mater. Interfaces 2013, 5, 3487.
- [67] A. C. van Popta, J. Cheng, J. C. Sit, M. J. Brett, J. Appl. Phys. 2007, 102, 013517.
- [68] H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley, Z. H. Levine, *Phys. Rev. B* 2008, *78*, 205108.
- [69] A. Moreau, C. Ciracì, J. J. Mock, R. T. Hill, Q. Wang, B. J. Wiley, A. Chilkoti, D. R. Smith, *Nature* **2012**, *492*, 86.
- [70] Q. Zhang, W. Li, L. P. Wen, J. Chen, Y. Xia, Chemistry 2010, 16, 10234.
- [71] M. Uphoff, M. Brekenfeld, G. Rempe, S. Ritter, New J. Phys. 2015, 17, 013053.
- [72] H. Zhang, H. Chen, T. Zhang, X. Mi, Z. Jiang, Z. Zhou, L. Guo, M. Zhang, Z. Zhang, N. Liu, H. Xu, Nanoscale Adv. 2022, 4, 1145.
- [73] C. A. Reynaud, D. Duché, J. Le Rouzo, A. Nasser, L. Nony, F. Pourcin, O. Margeat, J. Ackermann, G. Berginc, C. A. Nijhuis, L. Escoubas, J.-J. Simon, Adv. Opt. Mater. 2018, 6, 1801177.
- [74] E. Oksenberg, I. Shlesinger, A. Xomalis, A. Baldi, J. J. Baumberg, A. F. Koenderink, E. C. Garnett, *Nat. Nanotechnol.* 2021, *16*, 1378.
- [75] K.-W. Tsai, K. Sivashanmugan, C.-H. Lin, P.-J. Tsai, S.-C. Cheng, Y.-C. Lan, T.-Y. Chen, T.-C. Wen, J. Taiwan Inst. Chem. Eng. 2016, 69, 146.
- [76] O. Christopher, G. Anand, S. Tapan, M. Catherine, Anal. Chem 2005, 77, 3261.
- [77] A. Zhang, X. Cao, M. Tang, Y. zheng, Z. Lu, Y. Shen, J. Appl. Polym. Sci. 2014, 131.
- [78] H. Chen, X. Kou, Z. Yang, W. Ni, J. Wang, Langmuir 2008, 24, 5233.
- [79] M. E. Dufond, J.-N. Chazalviel, L. Santinacci, J. Electrochem. Soc. 2021, 168, 031509.
- [80] A. Bakri, M. Sahdan, F. Adriyanto, N. Raship, N. Mohd Said, S. Abdullah, M. Rahim, AIP Conf. Proc. 2017, 1788, 030030.
- [81] A. Gomer, T. Bredow, ChemistryOpen 2022, 11, 202200077.