Electro-Optic Metasurfaces Based on Barium Titanate Nanoparticle Films

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Metal-oxides are promising candidates to substitute silicon in intra-chip optical interconnects, as they exhibit great electric field tuning capabilities. The development of crystal ion slicing of thin films from bulk crystals and the advances over epitaxial growth have allowed the integration of metal-oxides on a single chip. In terms of performance, they possess strong electro-optic response over broad bandwidths across near-infrared. However, lattice and thermal expansion coefficient mismatch limits the compatibility with available substrates and other materials, while physical hardness makes high quality nanostructures difficult to implement. Here, a novel concept of electro-optic (EO) switching is introduced: an adjacent BaTiO$_3$ nanoparticle film to a plasmonic metasurface provides reflection changes up to 0.15% under 4 V of control signal for modulation frequencies up to 20 MHz, in the near-infrared. The nanoparticle films show EO coefficients ($37.04 \pm 25.6 \text{ pm V}^{-1}$) comparable to lithium niobate crystals, are deposited uniformly over large scale and on any type of substrate, while retain optical nonlinear properties (e.g. second-harmonic generation). Photonic nanostructures such as metasurfaces incorporated with nanoparticle films can harness the multifunctional properties of metal-oxides such as BaTiO$_3$ to form a new family of switchable nano-devices across the entire visible to near-infrared part of the spectrum.

Barium titanate (BaTiO$_3$) is a metal-oxide material used in electronics as ceramic capacitor or as electronic memory element,[1] while in photonics as photorefractive or quadratic nonlinear bulk crystal.[2,3] The structure and the symmetry of the crystal have a significant impact over many physical properties of BaTiO$_3$.

Most interestingly, when the Ti$^{4+}$ cations are displaced with respect to the octahedra that O$^{2-}$ anions form, a permanent electric polarizability is present. Under such conditions the unit cell lacks an inversion symmetry center (non-centrosymmetric) and optically nonlinear effects appear, such as second-harmonic generation (SHG), described by the second-order susceptibility $\chi^{(2)}$. The nonlinear optical susceptibilities obtained by SHG measurements determine the electronic contribution to the electro-optic (EO) coefficient. For lower frequencies than optical, the EO response stems from the phonon-electron coupling producing a considerable change of the refractive index upon the application of electric fields.[5] The control of BaTiO$_3$ refractive index upon electrical stimuli provides a multifunctional material platform to realize active nano-devices. The bulk BaTiO$_3$ crystal has typical EO coefficients of the order of hundreds of pm V$^{-1}$, in near-infrared.[6] However, the integration of BaTiO$_3$ thin films on a single chip remains challenging, as its growth on silicon is hampered by the mismatched crystal structure and chemical properties. Albeit the progress reported on the epitaxial growth of BaTiO$_3$ to produce electro-optic devices out of thin films and waveguides,[7–10] there are limited reports on the electro-optic behavior of BaTiO$_3$ with nanophotonic platforms such as metasurfaces.

The research over EO materials has been a long-standing effort to increase the bandwidth and the depth of modulation as well as to minimize the power requirements and interaction length of the EO devices. Among these systems, non-centrosymmetric crystals,[11] heavily doped semiconductors,[12,13] liquid crystals,[14] nano-mechanical systems,[15] and electro-active polymers,[16] are the main schemes to deliver electro-optic responses in the near-infrared. Carrier dispersion effects of heavily doped semiconductors are limited by the optical losses and lifetime of the carriers. Schemes based on nano-mechanical and/or liquid crystal systems are only responsive to DC or few microseconds electrical signals,[15,17] while EO polymers suffer from chemical and thermal stability. In contrast, electro-optic response of non-centrosymmetric metal-oxide materials such as BaTiO$_3$ is based on the intrinsically low loss and ultrafast Pockels effect.

The research of high index dielectric nanoparticles has been driven by several schemes related with nano-opto-mechanical
BaTiO$_3$ nanoparticles due to the large optical bandgap and refractive index support Mie-type of optical resonances employed in wavelength conversion for particle size comparable to the excitation wavelength. More interestingly, nanoparticles suspended in solution can be deposited via wet deposition means. For example, spin coating, drop cast, spray pyrolysis, and form uniform thin films with application ranging from sensing and energy harvesting up to nonlinear optics.

Here, we design and fabricate a plasmonic nanosurface that support optical resonances in the near-infrared. It is formed by a subwavelength, periodic grating of gold (Au) nanowires coated with a thin layer (200 nm) of BaTiO$_3$ nanoparticles. Every pair of the Au nanowires is connected on a different electrical terminal; thereby the BaTiO$_3$ nanoparticles between each pair of Au nanowires can be subject to electric actuation. The nanoparticles are deposited by wet process, which form thin films of nanoscale thickness with large uniformity. Aqueous solution of 50 nm BaTiO$_3$ nanoparticles is spin coated on silicon and gold offering a simple, scalable, and large-scale deposition method. The thickness uniformity over large scale of BaTiO$_3$ nanoparticle films is verified by the thickness dependent uniform colors produced upon deposition on silicon substrates. We characterize the refractive index of the nanoparticle film with the use of angle-resolved reflectometry and verify the non-centrosymmetric crystal structure of the BaTiO$_3$ by SHG measurements. Then, the EO response of the plasmonic nanostructure covered with the BaTiO$_3$ nanoparticles is tested. The nanoparticle film can dynamically tune the optical reflection of the metasurface (at 1064 nm), when it is driven by electric pulses as short as tens of nanoseconds. An equivalent electro-optic coefficient of the nanoparticle films developed here is also extracted (37 pm V$^{-1}$), showing response comparable to commercial EO modulators made of LiNbO$_3$ bulk crystals.

Aqueous solution with 25 wt% concentration of BaTiO$_3$ nanoparticles is spin coated on chemically cleaned and plasma-treated single side polished silicon wafers. The average nanoparticle diameter is 50 nm. Figure 1a–d show different coloration of silicon wafers upon deposition of BaTiO$_3$ nanoparticles thin films of different thickness. The nanoparticle solution subjected to spin-coating of 800, 1000, 2000, and 4000 revolutions per minute (rpm), produce films of 477, 430, 307, and 246 nm thick, respectively. A bare silicon wafer is also shown for comparison. The refractive index of nanoparticle films is characterized by angle-resolved reflectometry and verify the non-centrosymmetric crystal structure of the BaTiO$_3$ by SHG measurements. Therefore, we perform SHG measurements on the BaTiO$_3$ nanoparticles to verify the non-centrosymmetric crystal structure of the particles. The tetragonal distortion ($\delta$) of BaTiO$_3$ is defined as the ratio $\delta = (c - a)/a$, where $c$ and $a$ are the length of c-axis and a-axis, respectively. Distortion ($\delta$) is only 1% in bulk crystals, as a result X-ray diffraction (XRD) measurement of nanoparticles is difficult to identify the crystal structure, due to the line broadening effect. XRD data of the BaTiO$_3$ nanoparticles used in this experiment are presented in the Supporting Information section. Therefore, we perform SHG measurements on the BaTiO$_3$ nanoparticles to verify the non-centrosymmetric nature of the particles.
phase. Previous studies show that BaTiO$_3$ nanoparticles possess the tetragonal phase for particle size larger than 30 nm.$^{[10]}$ Furthermore, the closely packed distribution of nanoparticles suppress contribution from surface effects to the SHG signal, similar to isolated BaTiO$_3$ nanoparticles in matching refractive index medium.$^{[33]}$ Thus, the SHG signal can be a non-invasive method to identify the lack of inversion symmetry of the nanoparticle thin film. The polarization dependence of SHG signal produced by a thin film (200 nm) of BaTiO$_3$ nanoparticles on top of unstructured gold is presented in Figure 1g. The SHG signal recorded by a sCMOS camera and then averaged over the area of the beam size (green area Figure 1g), namely 4 µm. The dependency of the SHG signal over polarization verifies the existence of an elongated axis (c-axis) of the nanoparticles with considerable in-plane projection. Moreover, the polar plot of two smaller regimes (≈50–70 nm) of the SHG signal (blue and red star in Figure 1g) show much sharper polar dependence, as a result of the less diverging c-axis orientation.$^{[32]}$ More details for the SHG measurements are presented in the experimental section.

To harness the electro-optic response of BaTiO$_3$ nanoparticle films, we develop a device structure, where an array of plasmonic gold (Au) nanowires is covered with a thin layer of BaTiO$_3$ nanoparticles. Each pair of nanowires is connected alternately to two electrical terminals on opposite sides of the device and permit the electrical actuation of the BaTiO$_3$ nanoparticles. The device geometry is shown by a scanning electron microscopy (SEM) image in Figure 2a,b with total dimensions of 25 µm × 12 µm. (For more fabrication details see in Experimental Section.) In such configuration, the periodic array of Au nanowires supports plasmonic resonances outside gold and within the BaTiO$_3$ nanoparticle film. Air gaps between the particles are deeply subwavelength; as such, they cannot modify the nature of the plasmonic resonance supported by the Au nanowires.

The spectral position of the optical resonances supported by the metasurface is determined by the geometry of the plasmonic nanowires, as well as the refractive index of the surrounding medium. We design the metasurface with period, $P =$ 550 nm and slot size $s =$ 175 nm as seen from the cross section SEM image in Figure 2c. These parameters are chosen to produce a highly sensitive photonic metasurface upon the refractive index change of the surrounding medium, at the wavelength of the probe laser. This optical resonance is based upon a spatial distribution of the electric field that generates magnetic dipole-like resonances within each slot (s) as illustrated by the numerically simulated cross-sectional field maps in Figure 2d.

Normal incidence reflection spectra for the metasurface are measured using an infrared imaging spectrometer upon light illumination of the sample with a broadband light source, (more details are shown in the Experimental Section). For incident light polarized perpendicular to the nanowires (the transverse magnetic or TM mode of illumination), the metasurface supports an optical resonance with a reflection minima at 1100 nm red dashed line (Figure 3a) with a quality factor ($Q$) of ≈10 ($\Delta \lambda / \Delta \lambda = 1100/1150–1060$, where $\lambda _r$ is the resonance frequency and $\Delta \lambda$ is the half-maximum linewidth). This reflection spectrum can be understood as the interference between the plasmon resonance excited in the nanostructure and the optical field of the incoming plane wave. Around 1100 nm, the optical fields interfere destructively and reduce the far field reflection characteristics of the metasurface. The optical response is polarization dependent, where no resonant response is recorded for polarized light parallel to the nanowires, as reported in several plasmonic nano-gratings.$^{[13]}$ The extinction spectra from the nanoparticle film is also presented in Figure 3a. The optical losses
are associated with the roughness of the nanoparticle film and are less than 7%.

Furthermore, we simulate the reflection spectra of the plasmonic metasurface based on the geometric properties of the metasurface presented in Figure 2. Metasurface optical reflection for three different values of the refractive index of the BaTiO$_3$ nanoparticle film ($n_{\text{BTO}}$) are presented in Figure 3a. In this scenario, the optical resonance is blue-shifted as the value of $n_{\text{BTO}}$ decreases, therefore a reflection change at the 1064 nm probe wavelength is expected. More specifically, at 1064 nm the $n_{\text{BTO}}$ alters the metasurface reflection by $\Delta R = 15\%$ upon 0.1 change of $n_{\text{BTO}}$. Minor discrepancies between experimental and simulated spectra are attributed to manufacturing imperfections; such as deviation from the ideal model geometry, for example, over-milling of nanowire array into the substrate and the rounded cross-sectional profile of milled nanowires, stoichiometric change of the Au nanowires during focused ion beam (FIB) milling, which may modify refractive index. However, BaTiO$_3$ nanoparticle film is deposited after FIB milling, and thereby remains intact from ion bombardment that could induce any modification in the physical properties of BaTiO$_3$. Strong overlap between the optical and the electrical mode inside the BaTiO$_3$ is necessary in order to maximize the electro-optic coupling.\[8\] We numerically simulate the cross-sectional map in the y-z plane of the static electric field amplitude over a single period of the nanowire array for a gap size of 175 nm and an applied bias difference of 1 V between two Au nanowires, using finite element method calculations. The color map of the electric field distribution is presented in Figure 3b, the E-field is maximizing between the Au nanowires, where the BaTiO$_3$ nanoparticles are. Model details are given in the Experimental Section. In vivid contrast to dielectric waveguides, where the electrodes distance is associated to the propagation losses of the device, the electrodes distance in electro-optic metasurfaces can be reduced significantly and therefore minimize actuation voltage. Nevertheless, the electrode distance will modify the optical near field confinement, therefore opens a new platform to engineer the electro-optic coupling based on the plethora of optical modes that photonic metasurfaces support.

We exploit the dynamic electro-optic response of the metasurface in the near-infrared wavelength of 1064 nm, which is adequate for several pulsed-laser systems with applications in telecommunication networks, medicine, and optical tweezers. Figure 4a shows the schematic of the electro-optic setup used to measure the reflectivity change of the metasurface over the application of a DC offset and AC electric signals. A fiber coupled diode laser launches a continuous wave (CW) laser beam on a polarization-maintaining (PM) fiber at the central wavelength of 1064 nm. The laser beam after passing the fiberized circulator is exiting the fiber, where a pair of lenses are used first to collimate and then focus on the sample. Between them, a half-wave plate controls the polarization state of the laser beam. The fiber circulator is used to guide the reflected signal from the EO metasurface into an InGaAs amplified photodiode, where the electronic signal is detected via a lock-in amplifier at the modulation frequency used to electrically drive the sample. In order to define the bias point that maximizes the EO modulation from the nanoparticle film, we fix the AC signal at 5 MHz and the peak-to-peak amplitude at 4 V. Then, we scan the DC offset from -4 V to 4 V, in steps of 200 mV, the results are shown in Figure 4b. On the top horizontal axis, we plot the DC offset electric field strength in units of MV/m as estimated from simulation data of Figure 3b, while the bottom axis shows the experimental DC offset in volts. The graph shows a hysteretic behavior after decreasing/increasing the bias field applied on the nanoparticle film. For voltages higher than 4 V (13.2 MV m$^{-1}$) the nanoparticle film do not improve the modulation depth of the reflected signal. Then, we perform a scan over the driving AC frequency, for a fixed DC signal of 4 V, while we keep applying a sinusoidal AC signal with peak-to-peak amplitude of 4 V from 500 kHz up to 20 MHz as shown in Figure 4c. The reflectivity modulation is steady over this frequency range at the level of 0.15%. We also present the response from the Au nanowire array without the nanoparticle thin film on top. The signal recorded corresponds to the noise level of our system and quantifies the minimum reflection change that can be detected. Furthermore, we tune the polarization axis of the linearly polarized light, with the use of a half-wave plate. The electro-optic response is highly birefringent with the maximum modulation achieved for the polarization of light being perpendicular to the nanowires, see Figure 4d. A sinusoidal function (black dashed line) is used for fitting with experimental data (green circles).
In order to compare the electro-optic performance of the BaTiO3 nanoparticle film with existing electro-optic crystals, we estimate the refractive index change of the BaTiO3 layer based on the reflection change that we recorded experimentally. Finite element method simulations show that the metasurface reflectivity change at 1064 nm corresponds in a refractive index change of the BaTiO3 nanoparticle film of $\Delta n = 9.9 \times 10^{-4}$. Thus, the electro-optic coefficient of the metasurface can be estimated based on the formula:

$$ r_n = nE = 37.04 \pm 25.6 \text{ pm V}^{-1} $$

where $E$ is the applied electric field, $\Delta n$ is the electrically actuated refractive index change of the film, and $n$ is the refractive index of the film. We cannot probe the tensorial nature of BaTiO3 electro-optic coefficient, as the deposition method we follow does not control the orientation of the nanoparticles. The EO response detected here is lower than the bulk BaTiO3. As a result, we expect an improvement on the electro-optic response if special treatment like capillary assembly of nanoparticles or crystallographic alignment of nanoparticles during self-assembly is achieved.\(^{[35,36]}\) However, the electro-optic response detected is already comparable to bulk electro-optic LiNbO3 crystals, while further optimized design of metasurface can translate the electro-optic response of BaTiO3 nanoparticle film in even higher modulation depths. The electro-optic effect of BaTiO3 nanoparticles relies on the tetragonal phase of the crystal. In BaTiO3 nanoparticles larger than 30 nm the tetragonal phase exists.\(^{[30]}\) Here, we use nanoparticles of 50 nm in diameter, however larger nanoparticles are expected to enhance further the electro-optic modulation contrast, since they can support larger single crystal domains. For the metasurface design proposed here, nanoparticles up to 175 nm in diameter (as much as the space between two neighboring nanowires is) may be employed to induce stronger reflectivity modulation contrast. BaTiO3 nanoparticles have negligible EO response for a zero bias voltage as it is shown in Figure 3b. The strong electro-optic modulation manifests only under intense static electric field strength of several MV m\(^{-1}\), where nanoparticle polarizability aligns along the E-field. The inherent optical nonlinearity and EO response that metal-oxides possess can form a new family of active metasurfaces by electrically controlling the dielectric environment of plasmonic and/or dielectric nanostructures with large impact in their optical properties.\(^{[37]}\) The scalability of the solution-processed nanoparticle films...
produced here is highly dependent on the chemical properties of the substrate such as hydrophilicity, as well as the solubility and suspension of the nanoparticle solution. Multi-layer metasurfaces can be made by repeating spin-coating steps or by incorporating standard lithographic techniques followed by a single spin coating step, thus realizing metasurfaces over several centimetres. Recently, it has been shown that multi-layer nanostructures can be produced by BaTiO$_3$ nanoparticles and UV-soft nanoimprint lithography over a surface area of more than 1 cm$^2$.[27] Measurements like reciprocal space maps and poling figures may elaborate further the electro-optic response of these nanoparticle films. Recent reports on polycrystalline thin films deposited on silicon also show EO response, such as lead zirconate titanate.[138] We speculate that thermal expansion mismatch between substrates and films can be a possible mechanism to induce a preferential orientation on poly-films of this type.

In conclusion, we show that the deposition of metal-oxide thin films is feasible from solution of BaTiO$_3$ nanoparticles on any substrate. The films retain their uniformity over large-scale areas, yielding vibrant colors upon illumination with natural light under oblique view. The crystal structure of the nanoparticles remain non-centrosymmetric as tested with SHG measurements. At the same time, the nanoparticle film when is deposited on top of resonant nanostructures can control dynamically the optical properties of a plasmonic metasurface via the EO effect and thereby perform EO switching at sub-wavelength interaction lengths. The electrode design permit the low actuation voltage of the BaTiO$_3$ films, while the deposition of the particles on a pre-patterned Au keep properties of the EO film intact from stoichiometric or chemical modification. Photonic metasurfaces with tunable optical response by design, can serve as electro-optic modulators incorporated with BaTiO$_3$ nanoparticle films across the entire visible to near-infrared part of the spectrum for applications that require modulation at megahertz frequencies, such as mode-locking.

**Experimental Section**

**Nanoparticle Angle-Resolved Reflectometry:** The angle resolved reflectometry realized in a nanoparticle film of 538 nm thickness. Four laser wavelengths were used: 405, 526, 636, and 983 nm. A weakly dispersive refractive index was measured. A Cauchy fit was used to extract the value at the wavelength of 1064 nm, Figure 1f. A laser beam on a rotating stage illuminated the nanoparticle film over a range of angles, while a prism coupler was used in contact with the sample and guided the light to the film. At specific angles, laser light propagated inside the nanoparticle film due to the excitation of guided propagation modes, Figure 5.[39] As a result, a sharp drop of the laser intensity was recorded at the photodetector. Thickness and refractive index of the film were measured independently, as the incident angle of the first mode (reflection dip) determined film refractive index, while the angular difference between the modes determined the thickness of the film. The angle-dependent intensity measured on the reflectometric setup was shown at the wavelength of 636 nm, Figure 5b.

**Nanoparticle Thin Film Preparation:** After 5 min of ultrasonication of the aqueous solution of 25 wt% concentration of BaTiO$_3$ nanoparticles (dispersion in water from Nyacol Nano Technology Inc., tetragonal phase, 50 nm diameter), 3 µL of the functionalized BaTiO$_3$ was deposited onto pre-cleaned substrates. Silicon substrates were treated first with piranha and then with nitrogen treatment for 2 min to improve the uniform deposition of the films. The spin coating speed was varied between 800 and 4000 rpm over 3 min for the films deposited on silicon and 3000 rpm for the samples deposited on gold. Ozone treatment on the gold surface prior nanoparticle deposition was used to improve the uniformity of the nanoparticle films on the pre-patterned gold. Thickness of the films was measured via profilometry, where surface roughness from each sample shown in Figure 1a–d is: 9.6, 9.2, 15.3, and 12.4 nm, respectively.

**Figure 5. Refractive index and guided modes of BaTiO$_3$ nanoparticle films.** a) Schematic of the angle-resolved reflectometric characterization of nanoparticle films: guided modes supported at specific angles, allow the determination of thickness and refractive index of the thin film. Inset: SEM cross section image of nanoparticles. b) Reflection intensity over several angles of illumination of a BaTiO$_3$ nanoparticle film deposited on silicon.

**BaTiO$_3$ Nanoparticle Metasurfaces:** Periodic arrays of gold nanowires were fabricated by FIB milling. A Ga$^+$ ion source used to mill Au films of 200 nm thickness. The acceleration voltage and the current density of the ion source were 30 keV and 28 pA, respectively. The pattern of electrodes required to alternately bias nanowires (as indicated in Figure 2b) and separate each side of the device into two electrical terminals. Deposition of 200 nm gold realized with an e-beam evaporation system, on quartz substrates.

**Second-Harmonic Generation Measurements:** A home-built nonlinear optical microscope in the reflection mode had been used.[40] The laser source is a tunable Ti:Sapphire femtosecond pulse laser tuned for emission at 1050 nm. The pulse width was 140 fs, while the repetition rate was 80 MHz. The laser beam was focused on the sample with the use of a 50x objective and the SHG signal was collected with the same objective and focused to CMOS camera to get the SHG signal images, thus the SHG signal from the blue and red curve corresponded to the SHG intensity recorded by two different pixels of the camera. Accordingly, for the green curve the signal from several pixels of the camera was averaged. The laser beam was filtered out with two FESH900 filters (cutoff wavelength: 900 nm). The power of incoming light was controlled by a half-wave plate and a polarizing beam splitter, with an additional half-wave plate used to control the polarization of the excitation laser. Images of the SHG intensities by varying the polarization of the incident laser beam from 0° to 360° with steps of 10° was recorded. For each polarization, a single SHG image was recorded.

**Numerical Simulations:** Full-wave electromagnetic simulations of the metasurface structure, based on the geometry presented in Figure 2b, are performed using the finite element method of COMSOL Multiphysics. Calculations employed periodic boundary conditions in the y-direction and infinitely long nanowires in x-direction. Unit cell period: 550 nm,
gap size: 175 nm, gold thickness: 200 nm and 300 nm total thickness of the metasurface. The refractive indices for Au and BaTiO$_3$ nanoparticles films were obtained from ellipsometric measurements. For metasurface, excitation was assumed normally incident, narrowband, and linearly polarized plane wave illumination. The roughness of the nanoparticle film resulted in scattering losses that contributed to an imaginary part of the nanoparticle films. The absorption coefficient of a thin film is: 
\[ \alpha = 2.303 \cdot A/k, \]
where \( A \) is the measured 7% absorption and \( k \) is the thickness of the nanoparticle films (200 nm), while the imaginary part \( k \) of BTO films is associated with the absorption coefficient with the following relation: 
\[ \alpha = (4\pi \cdot k) / \lambda, \]
where \( \lambda \) is 10$^{-6}$ m. Thus, imaginary part of BTO film is estimated to be: \( k = 0.064 \).

The electrostatic field distribution as presented in Figure 3b was modeled using the AC/DC COMSOL module, assuming a pair of parallel, 25 \( \mu \)m long wires, with a gold nanowire held uniformly at a given bias voltage against the other at 0 V (ground). The permittivity of BaTiO$_3$ nanoparticle film was assumed to be 50.$^{[14]}$

Spectroscopic Measurements: Reflection spectra (Figure 3a) were obtained using an infrared camera connected with a spectrometer, a 20 \( \times \) 20 \( \mu \)m sampling aperture was used while a 50 \( \times \) objective was used to focus and collect the reflected signal from a linearly polarized halogen lamp. Data were normalized to reference levels of a silver mirror (high reflector) and averaged over 15 repeated measurement cycles, each with a 20 ms integration time.

High-Frequency EO Modulation Measurements: The metasurface sample was connected to a function generator, which was used to apply an electric signal to the metasurface terminals. Optical reflection was monitored at the wavelength of 1064 nm using a diode laser providing an intensity of 100 \( \mu \)W cm$^{-2}$ at the sample. An InGaAs photodetector connected to the circulator, received the reflected optical signal from the sample. Lock-in amplifier recorded an electrical signal at the modulation frequency of the sample. Data were averaged over 20 consequent measurements at each setting of bias voltage.

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.

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