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We demonstrate an electrolyte-based voltage tunable vanadium dioxide (VO₂) memory metasurface. Large spatial scale, low voltage, non-volatile switching of terahertz (THz) metasurface resonances is achieved through voltage application using an ionic gel to drive the insulator-to-metal transition in an underlying VO₂ layer. Positive and negative voltage application can selectively tune the metasurface resonance into the “off” or “on” state by pushing the VO₂ into a more conductive or insulating regime respectively. Compared to graphene based control devices, the relatively long saturation time of resonance modification in VO₂ based devices suggests that this voltage-induced switching originates primarily from electrochemical effects related to oxygen migration across the electrolyte–VO₂ interface. © 2014 AIP Publishing LLC.

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In strongly correlated electron materials, competing spin, orbital, and lattice interactions result in complex phase diagrams. This complexity enables wide tunability of material properties in response to relatively weak external stimuli. A potent example is the direct modification of carrier density properties in response to relatively weak external stimuli. Among the various electric field effect techniques, electrolyte gating has created enormous interest due to its potential for high sheet-carrier-densities. For example, it has been shown that in NdNiO₃, LaCaMnO₃, SrTiO₃, and superconductors, electrostatic modification through electrolyte gating allows for tuning of the conductivity as well as the insulator-to-metal, magnetic, and/or superconducting phase transition temperatures. However, voltage-induced switching is not restricted to electrostatic tuning but can also stem from electrochemical modification. Electrochemical effects have already been explored and exploited by the microelectronics community. For example, switchable semiconductors such as WOₓ, TaOₓ, and TiOₓ have created a new generation of resistive memory (ReRAM) devices that may emerge as an alternative to silicon-based integrated circuit technology. While the condensed matter community has extensively researched the “clean” physics of intrinsic electrostatic doping, electrochemical sample modification has found its own place in electric field controlled nonvolatile switching applications.

In this study, we report on electrolyte-enabled experiments using two different THz photonic devices: (1) an array of split ring resonators (SRR) covered with a single layer of graphene grown using chemical vapor deposition (CVD) shown in the inset of Fig. 2(a), (2) the VO₂ hybrid metasurface shown in the inset of Fig. 2(b). We found that electrolyte gating can be used to control the resonant response of both of these devices. Specifically, we were able to achieve reproducible and reversible ambipolar modification of each device’s THz optical response.

We make our THz transmissive ion gel by mixing ionic liquid EMIM-TFSI with copolymer P(VDF-HFP) with a weight ratio of 1:4, following Ref. 5. We apply a ∼50–μm thick layer of ion gel to our devices as illustrated in Fig. 1. This thin ion gel has minimal THz absorption and is, therefore, ideal for long wavelength transmission measurements. Transmission through this film is nearly temperature independent in our investigation varying by less than 2%. Each device is probed using THz time domain spectroscopy and is placed in high vacuum prior to voltage application. The switchable area of these devices is approximately 10 × 5 mm², which is sufficient for most THz-based applications.

We first summarize our observations of gating effects on the graphene based metasurface response. Electrolyte gating of this graphene device is expected to cause solely electrostatic modification of the carrier concentration of graphene due to its excellent chemical stability. The rising conductivity in graphene near the SRR gap is expected to progressively damp and ultimately short the LC resonant response of the device with increasing voltage. This resonance originates from the capacitive nature of the SRR gap and inductive nature of the SRR loop forming an effective LC circuit. The electrolyte gating response in one of the graphene metasurfaces is shown in Fig. 2(a) for several voltages given by \( V = V_{\text{gate}} - V_{\text{CNP}} \), where \( V_{\text{CNP}} \) is the voltage of the charge neutrality point (CNP) (in our case \( V_{\text{CNP}} = -1.2 \) V) at which the conductance of graphene is minimized. All spectra in Fig. 2(a) are normalized to the transmission at \( V_{\text{CNP}} \). Due to the ambipolar nature of graphene, it is expected that the
metasurface response should be symmetric for hole and electron doping. Our measurements are in accord with this expectation: the spectra for \( V = -1.7 \text{ V} \) and \( +1.7 \text{ V} \) are equidistant from the CNP, and display nearly identical frequency dependence. In contrast, the spectrum obtained at \( 0.7 \text{ V} \) above \( V_{\text{CNP}} \) displays a response much closer to that of charge neutral graphene. We found that in gating of graphene, saturation of THz responses occurs within approximately 2 min of voltage application and the gating effect is fully reversible after the gate voltage is turned off. The 2-min saturation time of electrostatic doping in the graphene metasurface is a consequence of a relatively low diffusion coefficient of cation and anion motion in the ionic gel and the large functional area of the gating devices. Switching was possible on graphene devices as large as \( 1 \text{ cm}^2 \). Since we probe our samples optically, we minimize the resistive heating of our devices, which can be a problem in transport measurements where a source-drain voltage is applied.

Next, we examine the voltage-dependent response of our \( \text{VO}_2 \) based device. \( \text{VO}_2 \) is a canonical insulator-metal phase transition (IMT) material.\textsuperscript{22–28} When the temperature is increased above \( 340 \text{ K} (T_{\text{IMT}}) \), the \( \text{VO}_2 \) conductivity increases by several orders of magnitude with a simultaneous increase in the permittivity. As mentioned above, we elect to use voltage across the interface between the film and electrolyte, as opposed to temperature, to induce the \( \text{VO}_2 \) IMT in our 90 nm sol-gel \( \text{VO}_2 \) film. We characterize our device response to voltage application at two different temperatures. We first fixed the device temperature at \( 315 \text{ K} \), below the IMT hysteresis as shown in the inset of Fig. 3(a). Second, we keep the device within the hysteretic region of the IMT at a temperature of \( 336 \text{ K} \) (inset of Fig. 3(b)). We start by summarizing the results of our voltage-induced experiments before giving a full analysis of the device at each of these temperatures. Positive voltage applied to the gold gate in pristine samples below \( T_{\text{IMT}} \) increases \( \text{VO}_2 \) metallicity, thereby switching off the SRR resonance. Negative voltages applied in the hysteretic region of the transition exhibit a delay on the order of 2 min in which the \( \text{VO}_2 \) conductivity slightly increases, followed by a dramatic reduction of the \( \text{VO}_2 \) conductivity (Fig. 1(b)). Additionally, the effects of positive voltage application can be reversed using a negative bias, but do not reverse with only bias removal. Finally, the effects of negative voltages applied at elevated temperatures

![FIG. 1. (a) Schematic for electrolyte gating of graphene and \( \text{VO}_2 \) based metasurfaces. The area of the devices is \( \sim 1 \text{ cm}^2 \times 0.5 \text{ cm} \). The gold side gate has approximately the same area as the sample (green). Contacts for voltage application were fabricated with silver paint at a distance of \( \sim 5 \text{ mm} \) from each other. (b) Phase diagram for \( \text{VO}_2 \) including dependence on vanadium oxidation state. Black line across the figure indicates the phase boundary between the insulating state and metallic state, around which the conductivity of metallic state is maximized. The dashed portion of the black line indicates inconsistent results between published sources. Our results in Figs. 2(b) and 3 are indicated by the red and pink solid arrows. The two red dashed arrows indicate our explanation for the results by Jeong et al. (Ref 32).](image-url)

![FIG. 2. (a) Voltage dependent THz transmission with a graphene-metasurface structure. Spectra are taken \( \sim 2 \text{ min} \) after voltage application when gating effects saturate \( (V = V_{\text{CNP}} - V_{\text{SRR}}) \) and are normalized to THz transmission through graphene at the charge neutral point \( (V_{\text{CNP}} = -1.2 \text{ V}) \). (b) Voltage dependent THz transmission at \( 315 \text{ K} \) \( (V = V_{\text{SRR}}) \). Spectra are taken \( \sim 20 \text{ min} \) after voltage application and normalized to THz transmission through air. The insets in (a) and (b) show photos of the gold SRR sitting beneath (on) graphene (\( \text{VO}_2 \)) before the ionic gel is applied. The dimensions of the single SRR unit cell are also shown.](image-url)
near the phase transition are self-reversing after the voltage is removed.

We now analyze the THz transmission and the effects of electrolyte modification on the VO$_2$ metasurface at 315 K. The transmission spectra shown in Figure 2(b) illustrate the changes to the metasurface response with positive voltages. Initially, at 0 V, the device displays a strong LC SRR resonance (similar to that seen in the graphene device), indicating that the VO$_2$ is in its insulating state and is well below the hysteretic region of the IMT. The overall slope seen in these spectra is a result of absorption by the ion gel, which decreases with increasing frequency. Changes in the resonant response of VO$_2$ hybrid devices arise directly from modification of the permittivity and conductivity of VO$_2$, which cause a redshift and damping of the SRR resonance, respectively. Application of positive voltages monotonically drives VO$_2$ across the IMT following the pink solid line in Fig. 1(b), which shows the oxidation state dependent conductance of VO$_2$.

To explore the underlying mechanism and compare to the voltage induced changes in the graphene-based devices, we performed time dependent measurement in our VO$_2$ based devices. Figure 3(a) shows the time dependent normalized transmission at the resonance frequency at 315 K for various voltages. These data correspond to the spectra in Fig. 2(b). The transmission at the resonance frequency continually increases with fixed positive bias, and the rate of this increase is greater for larger biases. After application of the maximum voltage of 3 V, the sample remained in the metallic state and the metasurface resonance remained damped even after 24 h at zero bias, provided the device was kept in vacuum. To reverse this change in VO$_2$ properties, application of a negative voltage was necessary to restore the resonance. Similar time dependent gating effects were observed when resetting the transmission of the devices with negative bias (not shown). This on/off switching of the SRR with oxidation/reduction of vanadium enables memory tuning of the device as reverse bias application is required to go back to the original state. Through modification of the duration and polarity of the applied voltage, one can precisely control the on-resonance transmission as well as the frequency of the metasurface resonance. This is in agreement with previous findings that positive voltages create oxygen vacancies and increase metallicity of VO$_2$ samples with non-self-healing reversibility.

For negative voltages, oxygen is added to the VO$_2$ film while removal of oxygen, as proposed in the diagram in Fig. 1(b), shows the corresponding temperatures at which data were taken indicated by the orange dots on the VO$_2$ temperature driven hysteresis curve.

![Figure 3](image-url)

**FIG. 3.** (a) Time dependent on resonance transmission change $T_{\text{on}}(t)$ with various positive voltages at 315 K. Transmission is normalized to 0 V data $T_{\text{on}}(0\text{~V})$ before time zero. At each fixed voltage (1 V, 2 V, and 3 V), the rate of transmission change is different. The gating effect is non-reversible after the voltage is turned off. (b) Time dependent normalized THz transmission of VO$_2$ metasurface structure at 336 K with the applied voltage fixed at −3 V. Initially, the transmission increases but then dramatically decreases. Reversibility is seen after the voltage is turned off. The insets in (a) and (b) show the corresponding temperatures at which data were taken indicated by the orange dots on the VO$_2$ temperature driven hysteresis curve.
For positive gate voltage, $\text{VO}_2 + 2xe^- \rightarrow \text{VO}_2-x + x\text{O}^{2-}$.

The oxidation (reduction) process undergone by our device with negative (positive) voltage application is shown by the solid blue (pink) arrow in Fig. 1(b). The diagonal black line (solid negative (positive) voltage application is shown by the solid oxidation (reduction) process undergone by our device with as indicated by the blue arrow. For comparison, previous results obtained on bare $\text{VO}_2$ on TiO$_2$ substrate at high and low temperatures by Jeong et al. (Ref. 28) have also been indicated by the red dashed arrows in Fig. 1(b).

In summary, we have demonstrated tunable metasurfaces via ionic gel based electrostatic and electrochemical effects. Both thermal and electrical tunability can be realized in our hybrid devices. This enables unprecedented control over the optical properties of these metasurfaces over a wide temperature range and sets the stage for the future use of electrolyte gating in THz photonic devices. Through integration of additional switching mechanisms and material properties such as light induced phase transitions and electronic anisotropy, transition metal oxides, additional functionalities can be realized with more sophisticated electrolyte gating structures.

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