Reconfigurable THz and Microwave Metamaterials Based on π-Conjugated Polymers

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***Abstract* — We demonstrate various types of reconfigurable metamaterials utilizing π-conjugated polymer in terahertz (THz) and microwave frequency ranges. Linear actuators made from heavily doped polypyrrole film are utilized to change the relative lateral position of two THz metasurfaces with a control voltage, and accordion-shaped origami actuators are used to change the distance between two microwave split-ring resonators (SRRs). In both cases this results in significant tunability of the metamaterial resonances with a change of bias voltage. SRR meta-atom made of rolled heavily doped polypyrrole film show tunable resonant characteristics under monochromatic continuous wave (CW) microwave pumping.**

***Index Terms* — Electromagnetic metamaterials, organic materials, polymer films.**

I. Introduction

In recent years, numerous studies have been carried out to develop novel types of metamaterials and metadevices [1]. In metamaterials, artificially designed subwavelength resonant structures (meta-atoms) such as split-ring resonator (SRR) play crucial roles in obtaining rich variety of unique responses to electromagnetic (EM) fields [2]. However, resonant characteristics of such SRRs usually restrict their working frequency only in a narrow range, therefore numerous attempts have been made to add tunability to metamaterials [1]. Based on the fact that resonant condition of meta-molecules can be controlled by relative position and/or orientation via near-field interaction between meta-atoms [3],[4], tunable metamaterials have been developed [5]-[7]. Here we show our recent results on the electro-active metadevices in terahertz (THz) and microwaves utilizing organic π-conjugated polymers [8]. Doped polypyrrole (PPy) film can be utilized as soft actuator since its volume can be controlled even in ambient air by applying low voltage of only a few Volts [9]-[11]. We have synthesized thin films of PPy doped with hexafluorophosphate (PF6) ions, PPy(PF6), and utilized them to fabricate linear and accordion-shaped origami actuators for electro-active THz and microwave metadevices. Heavily doped PPy(PF6) is also known to behave like a Drude-type metal in THz or lower frequencies [12],[13]. We demonstrate the rolled PPy(PF6) film can be utilized as soft SRR meta-atom which can open and close capacitive gap responding to the incident microwave pump signal.

II. Experiment

A. Electrochemical Polymerization of Heavily-Doped PPy(PF6) Films and Fabrication of Accordion-Shaped Origami Actuators and Rolled PPy(PF6) Film Meta-atom

Pyrrole monomer is purchased from Sigma-Aldrich and purified by distillation prior to use. PPy(PF6) films are electrochemically synthesized by the anodic oxidation of the pyrrole in the presence of PF6 ions. The polymerized PPy(PF6) films on the electrode are peeled off and then dried in vacuum.

For THz device, PPy(PF6) films are cut into small belts and used as linear actuators (Fig. 1(a)). For microwave tunable meta-molecules, PPy(PF6) films are cut into small strips and is made into an accordion shape by alternately folding each side of the strips (Fig. 1(b)). Rolled PPy(PF6) film is made during vacuum drying process after peeled off the electrode. Dried rolled film is cut into small stripes to obtain SRR meta-atom (Fig. 1(c)).

B. Fabrication of Tunable THz and Microwave Devices

The gold complementary electric split-ring resonators (CESRR) arrays are fabricated on quartz substrates by conventional optical lithography and a lift-off process (Fig. 1(a)). The two fabricated CESRR layers are placed face-to-

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face and PPy(PF6) film are attached to one of the freely movable CESRR array and thin copper wires are attached for voltage application.

We use copper SRR printed on Rogers R4003 dielectric substrates. The inner radius, track width, slit width and thickness of the SRRs are 3.2 mm, 1.0 mm, 0.2 mm and 0.035 mm, respectively. The dielectric constant and loss tangent of the dielectric substrate are 3.5 and 0.0027, and its thickness is 0.5 mm. Two of the SRRs on the dielectric substrate face each other with the SRR side out and the capacitive gaps oriented the same direction. Two accordion-shaped origami actuators are placed between them (Fig. 1(b)).

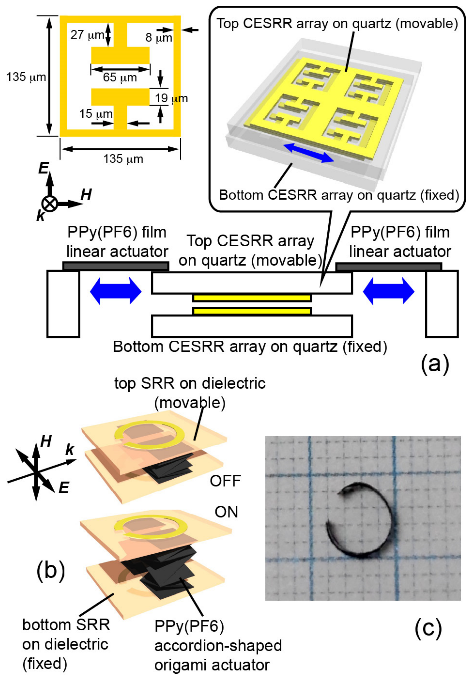

Fig. 1. (a) Schematics of the tunable THz device based on double-layered CESRR arrays with fixed substrate and movable superstrate suspended with PPy(PF6) linear actuator. (inset) Geometry of the CESRR unit cell along with the polarization directions of the incident THz wave. (b) Schematics of the tunable microwave device based on a pair of SRRs with PPy(PF6) accordion-shaped origami actuator along with the polarization directions of incident microwave. (c) Photograph of SRR meta-atom made of a rolled PPy(PF6) film.

C. THz and Microwave Transmission Measurement

Transmission spectra of THz metadevice are measured using a THz time-domain spectroscopy (THz-TDS) system. A wire-grid polarizer is inserted in front of the sample to select the polarization direction of the THz radiation aligned across the gaps of the CESRRs (Fig. 1(a)). The sampled time-domain transmission responses are time-windowed and are Fourier-transformed to obtain frequency domain spectra.

For microwave transmission measurements, the devices are placed in the center of a WR229 rectangular waveguide, in which only the fundamental (TE_{01}) mode can be supported in the frequency range of interest. The transmission spectra are measured using a vector network analyzer (Rohde and Schwarz ZVB-20).

III. Results and Discussions

A. THz Active Metasurfaces Utilizing PPy(PF6) Films as Linear Actuators

Fig. 2 shows transmission spectra of the tunable THz device based on double-layered CESRR arrays with PPy(PF6) linear actuator (Fig. 1 (a)) without and with applied voltage. It has been confirmed that by stacking these CESRR arrays, two resonant modes were observed at 0.318 THz and 0.468 THz. These two modes are symmetric and anti-symmetric modes corresponding to in phase and out of phase loop currents, respectively [6]. The well-aligned device shows resonance around 0.320 THz due to the symmetric mode (Fig. 2). We have successfully obtained a frequency shift of resonant THz transmission by applying a low bias voltage of only a few Volts. Such voltage leads to contraction of the polymer film, and this laterally shifts the CESRR layer (Fig. 2, inset). By turning off the applied voltage, the system recovers its initial state and transmission spectrum.

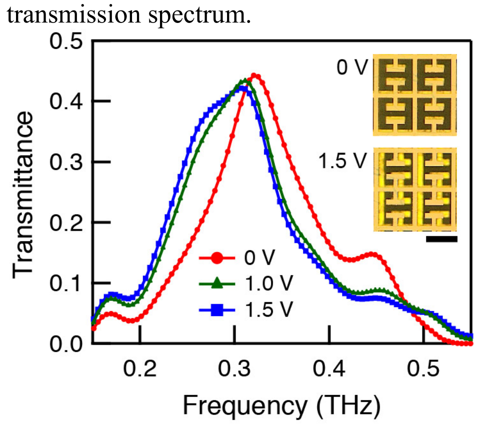

Fig. 2. Measured THz transmission spectra of the tunable THz device based on double-layered CESRR arrays with PPy(PF6) linear actuator without and with applied voltage. (inset) Optical microscope images of double-layered CESRR arrays without and with (1.5 V) applied voltage. Scale bar is 100 μm.

B. Microwave Active Metamolecules Utilizing Accordion-Shaped Origami Actuators Made of PPy(PF6) Films

Since the contraction of the PPy(PF6) film is only a few % and the typical size of meta-atom working at GHz frequencies should be in mm range, it is not realistic to utilize our film as a linear actuator. Therefore, we have developed accordion-shaped origami actuators from PPy(PF6) film, which show longer actuation length, and utilized them to control the distance between a pair of SRR meta-atoms (Fig. 1(b)). The working principle is based on unfolding of the creases and it can induce more than 100% elongation when actuated by only a few Volts [8]. It is known that the resonant frequencies of the two modes (symmetric and anti-symmetric) are sensitive to the relative orientation of SRRs and the spacing between them. Fig. 3 shows measured microwave transmission spectra of tunable microwave device based on PPy(PF6) accordion-shaped origami actuator under applied voltages. By increasing the applied voltage, the transmission dip shifts to a lower frequency and we have achieved 77 MHz of shift with 5.5 V.

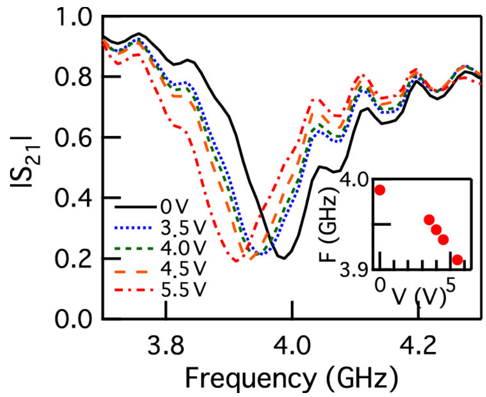

Fig. 3. Measured microwave transmission spectra of tunable microwave device based on PPy(PF6) accordion-shaped origami actuator under applied voltages. (inset) Applied voltage dependence of the resonant frequency of the device.

C. Microwave Meta-atom Utilizing Rolled PPy(PF6) Films

Fig. 4 shows measured microwave transmission spectra of SRR meta-atom made of rolled PPy(PF6) film. By increasing pumping microwave CW signal, transmission dip shifts to a higher frequency. The system does not recover initial state, therefore, further investigation is needed to develop tunable devices can be operated in a reversible manner.

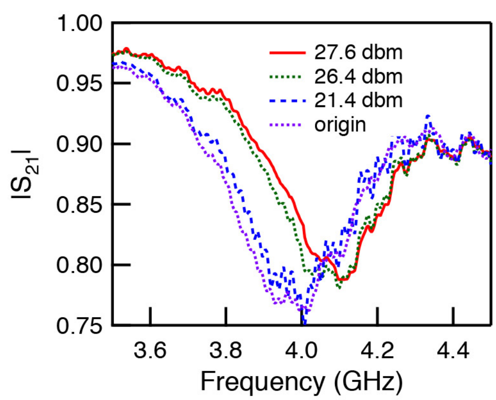

Fig. 4. Measured microwave transmission spectra of rolled PPy(PF6) film SRR meta-atom pumped with CW monochromatic microwave signal.

IV. Conclusion

We demonstrated various types of reconfigurable metamaterials utilizing π-conjugated polymer in THz and microwave frequency ranges. Linear actuators made from PPy(PF6) film were utilized to change the relative lateral position of two CESRRs with a control voltage, and accordion-shaped origami actuators were used to change the distance between two microwave SRRs. In both cases this results in significant tunability of the metamaterial resonances with a control voltage. SRR meta-atom made of rolled PPy(PF6) film show tunable resonant characteristics under monochromatic CW microwave pumping. Our approach may be utilized to develop novel types of reconfigurable metamaterials and metadevices.

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References

[1] N. I. Zheludev, and Y. S. Kivshar, "From metamaterials to metadevices," *Nature Materials*, vol. 11, no. 11, pp. 917-924, November 2012.

[2] J. B. Pendry, A. J. Holden, D. J. Robbins and W. J. Stewart, "Magnetism from Conductors, and Enhanced Non-Linear Phenomena," *IEEE Trans. Microwave Theor. Tech.*, vol. 47, no. 11, pp. 2075-2084, November 1999.

[3] M. Lapine, D. Powell, M. Gorkunov, I. Shadrivov, R. Marqués and Y. Kivshar, "Structural tunability in metamaterials," *Appl. Phys. Lett.*, vol. 95, no. 8, pp. 084105-1-3, August 2009.

[4] D. A. Powell, K. Hannam, I. V. Shadrivov and Y. S. Kivshar, "Near-field interaction of twisted split-ring resonators," *Phys. Rev. B*, vol. 83, no. 23, pp. 235420-1-6, June 2011.

[5] M. Liu, Y. Sun, D. A. Powell, I. V. Shadrivov, M. Lapine, R. C. McPhedran and Y. S. Kivshar, "Nonlinear response via intrinsic rotation in metamaterials," *Phys. Rev. B*, vol. 87, no. 23, pp. 235126-1-6, June 2013.

[6] T. Matsui, M. Liu, D. A. Powell, I. V. Shadrivov, and Y. S. Kivshar, "Electromagnetic tuning of resonant transmission in magnetoelastic metamaterials," *Appl. Phys. Lett.*, vol. 104, no. 16, pp. 161117-1-4, April 2014.

[7] L. Liu, W.-C. Chen, D. A. Powell, W. J. Padilla, F. Karouta, H. T. Hattori, D. N. Neshev, and I. V. Shadrivov, "Post-processing approach for tuning multi-layered metamaterials," *Appl. Phys. Lett.*, vol. 105, no. 15, pp. 151102-1-4, October 2014.

[8] T. Matsui, Y. Inose, D. A. Powell and I. V. Shadrivov, "Electroactive Tuning of Double-Layered Metamaterials Based on π-Conjugated Polymer Actuators," *Adv. Opt. Mater.*, vol. 4, pp. 135-140, January 2016.

[9] H. Okuzaki, T. Kunugi, "Adsorption-Induced Bending of Polypyrrole Films and Its Application to a Chemomechanical Rotor," *J. Polym. Sci. B Polym. Phys.*, vol. 34, no. 10, pp. 1747-1749, July 1996.

[10] H. Okuzaki, T. Kunugi, "Electrically Induced Contraction of Polypyrrole Film in Ambient Air," *J. Polym. Sci. B Polym. Phys.*, vol. 36, no. 9, pp. 1591-1594, July 1998.

[11] H. Okuzaki, T. Kuwabara, K. Funasaka, and T. Saido, "Humidity-sensitive polypyrrole films for electro-active polymer actuators," *Adv. Funct. Mater.*, vol. 23, no. 36, pp. 4400–4407, April 2013.

[12] T. Matsui, Z. V. Vardeny, A. Agrawal, A. Nahata, and R. Menon, "Resonantly-enhanced transmission through a periodic array of subwavelength apertures in heavily-doped conducting polymer films," *Appl. Phys. Lett.*, vol. 88, no. 7, pp. 071101-1-3, February 2006.
[13] T. Matsui, A. Agrawal, A. Nahata, R. Menon, Z. V. Vardeny, "Terahertz time-domain spectroscopy studies of subwavelength hole arrays in metallic films," *Physica B*, vol. 394, no. 2, pp. 363–367, May 2007