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An ultra-broadband single-component fractional-order capacitor using MoS₂-ferroelectric polymer composite

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The phase angle of a fractional-order capacitor's (FOC) impedance has a constant value between -90° and 0° . Maintaining this value over a broad frequency band is of utmost importance since it increases the applicability of the electrical circuit that employs the fractional-order capacitor (FOC). In this work, a molybdenum disulfide (MoS₂)-ferroelectric polymer composite is used to design/fabricate an FOC. The resulting FOC's bandwidth of operation, which is defined as the frequency band where the variation in the phase angle is no more than $\pm 4^\circ$, is five decades between 100 Hz and 10 MHz, a 3 decades improvement over the best reported state of the art. The value of the constant phase angle can be tuned from -80° to -58° by changing the type of the ferroelectric polymer in the composite and the volume ratio of MoS₂. The results presented in this work demonstrate the potential of the FOCs fabricated using MoS₂-ferroelectric polymer composites in robust and accurate realization of various electrical systems. *Published by AIP Publishing.*

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Over the last decade, there has been increasing interest in designing and fabricating fractional-order capacitors (FOCs) for various applications.^{1–11} Thanks to the additional parameter, namely, the fractional order (see [supplementary material](#) Sec. S1 and Fig. S1), FOCs offer increased flexibility in modeling and designing various electrical devices and systems, such as filters,^{12,13} oscillators,^{14,15} neural circuits,² transmission lines,¹⁶ supercapacitors and batteries,^{17–21} impedance matching networks,²² phase-locked loops,²³ and proportional–integral–derivative controllers,²⁴ and open the door to several unconventional properties that cannot be obtained using traditional circuit elements. For example, unlike a conventional capacitor, an FOC supports a capacitive memory, which enables temporal history of signals to be “stored” by electrical circuits, and therefore, it can be used to more accurately mimic/model electrical pulses communicated by neurons² and memory regeneration phenomena observed in dielectrics.^{25,26} Another example is the use of an FOC in a temperature controller instead of a conventional controller: The FOC reduces drastically both the overshoot amplitude and the time required to stabilize the temperature.⁷

One method of realizing an FOC in an electrical circuit is to represent it in terms of a chain network of resistors and capacitors (RC). The resulting circuit's overall impedance yields a transfer function with a non-integer order.^{27–29} However, oftentimes, the number of resistors and capacitors in the RC network is very high (adding an extra weight/cost to the system) and/or their resistance and capacitance values are impractical. To alleviate these bottlenecks, a method, which realizes the response of the RC network, using a

microscale structure consisting of polyvinylidene fluoride (PVDF) ferroelectric polymer composites embedding carbon-based nanomaterials, particularly reduced graphene oxide (rGO) sheets and multi-walled carbon nanotubes (MWCNTs), has been employed.^{1,3,30} The constant phase angle (CPA) of the impedance of an FOC, which is fabricated using any one of these composites, can be controlled by changing the volume ratio of the fillers and the type of polymer in the composite. It should be noted here that the term CPA comes from the assumption that the phase angle of the FOC's impedance remains unchanged in a frequency band. This frequency band is conveniently termed constant phase zone (CPZ). Even though the CPA of the FOCs fabricated using polymer composites is tunable, their CPZ has been limited to 2.5 decades, between 50 kHz and 10 MHz. It is clear that these FOCs are not suitable for many electronic systems, which work at low frequencies, such as fractional controllers⁷ and neural networks.^{2,31,32}

To alleviate this problem, in this work, an FOC is fabricated using PDVF polymer composites embedding molybdenum disulfide (MoS₂) nanosheets [see Fig. 1(a)]. The resulting FOC's CPZ is five decades wide changing from 100 Hz to 10 MHz [see Fig. 1(b)]. This is the largest bandwidth of operation that has been reported for an FOC so far.

MoS₂ belongs to the family of two dimensional (2D) transition metal dichalcogenide (TMD) materials with general formula MX₂, where M is a transition metal and X is a group VI element such as S, Se, and Te.^{33,34} A bulk MoS₂ material could be exfoliated into nanosheets by using a liquid solution to break the van der Waals forces between flakes.^{35,36} MoS₂ acts as a semiconductor; in addition, it has excellent mechanical properties. These properties render MoS₂-polymer composites (where MoS₂ is the filler) good candidates for fabricating electrical and optoelectronic devices.^{37–40}

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FIG. 1. FOC. (a) 3D schematics and (b) phase angle response of FOCs with PVDF-TrFE-CFE and MoS₂:PVDF-TrFE-CFE.

In this work, it is demonstrated that MoS₂-PVDF ferroelectric polymer composites result in a broadband CPZ when they are used to fabricate FOCs. This broadband response results from the cumulative effect of three mechanisms on the composite's electrical properties: Maxwell-Wagner-Sillars relaxation,^{41,42} the frequency-dependent phase angle of MoS₂ [due to its semiconducting nature⁴³ (see [supplementary material](#) Sec. S2, Figs. S2 and S3)], and dipolar relaxation of ferroelectric polymers.^{5,44} By carefully selecting the parameters of the composite, the spectra of these three mechanisms can be moved to overlap, which eventually yields a CPA with a broadband CPZ. The value of the CPA can be tuned by adjusting the volume ratio of MoS₂ and/or using a different type of ferroelectric polymer (since every ferroelectric polymer's dipolar relaxation frequency is different⁴⁴).

To prepare the composite, 200 mg Polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene (PVDF-TrFE-CFE) is dissolved in a 2 ml solvent, N, N-Dimethylformamide (DMF), under constant stirring at room temperature for two days to obtain 0.1 g/ml polymer solution. MoS₂ nanosheets are prepared from a powder which consists of MoS₂ particles with an average dimension of 2 μ m, using a solution phase exfoliation method.³⁵ First, MoS₂ powder is dispersed in DMF at a concentration of 20 mg/ml and stirred for 2 h using a tip-type sonicator (175 W, 35% amplitude, 10 s ON, 5 s OFF). Then, 80% of the solution is collected from top and the DMF is evaporated in a freezer dryer. Afterwards, MoS₂ nanosheets dispersed again in DMF at the desired concentration using an ultrasonication bath for 2 h, and the resulting solution is mixed with the PVDF-TrFE-CFE solution in proportion. The final mixture is first stirred for 24 h at room temperature and then further stirred for 1 h using a tip-type sonicator before drop casting. The composite solutions are drop-casted onto a 200 nm Au-deposited SiO₂/Si substrate and dried for 12 h at 110 $^{\circ}$ C under vacuum. A circular Au electrode with 3 mm diameter and 200 nm thickness is deposited using a shadow mask to permit the fabrication of nine individual FOCs on a 2 cm $\times$ 2 cm sample area. Finally, the sample is flip-bonded on a printed circuit board (PCB), so that each capacitor has a separate connection for the electrical measurements. Note that the thickness of the composite film can be tuned within the range of 20–60 μ m by varying the concentration of the cast solution.

The cross-sectional scanning electron microscopy (SEM) image of the composite film with $f_{\text{MoS}_2} = 0.25$ is

shown in Fig. 2(a). Here, f_{MoS_2} is the volume ratio of MoS₂ to the overall volume of the composite. The image shows that the MoS₂ nanosheets are distributed uniformly inside the composite. During the mixing process, the polymer chains wrap the MoS₂ nanosheets and avoid the aggregation of MoS₂. The transmission electron microscopy (TEM) image [Fig. 2(b)] shows an exfoliated MoS₂ nanosheet with a 1000 nm lateral size. The Fourier transform of the TEM image [inset of Fig. 2(b)] shows the clear hexagonal symmetry of the nanosheet. Furthermore, the comparison of X-ray diffraction (XRD) patterns of the composite film with $f_{\text{MoS}_2} = 0.25$ and the PVDF-TrFE-CFE film is provided in Fig. 2(c). Note that the XRD spectra are normalized with respect to the gold peak at 38 $^{\circ}$ for both structures. The XRD spectrum of the PVDF-TrFE-CFE film shows an intense peak at 18.2 $^{\circ}$ corresponding to a (111) plane. As expected, the composite film also exhibits a similar peak at 18.2 $^{\circ}$ but with a smaller amplitude as shown in the inset of Fig. 2(c). An additional peak is observed at 14.5 $^{\circ}$ in the spectrum of the composite film due to the (002) plane of MoS₂. This is consistent with the results that have been reported in the literature.⁴⁵ The XRD spectrum of the composite also confirms that no additional complex molecular structures are formed at the interface. Figure 2(d) shows the photographs of the flexible and rollable composite film and ready-to-use FOC, respectively.

Next, the performance of the FOCs fabricated using MoS₂:PVDF-TrFE-CFE composites with different f_{MoS_2} values is evaluated and compared to that of the state-of-art of FOCs fabricated using rGO:PVDF-TrFE-CFE and MWCNT:PVDF-TrFE-CFE composites (recipe in Ref. 3 is used to fabricate these composite films). An Agilent 4994A precision impedance analyzer with the 16048G fixture is used to measure the magnitude and phase angle of the FOCs' impedance in the frequency range between 100 Hz and 10 MHz. The amplitude of the applied voltage is 500 mV. The thickness of all films used for fabricating the FOCs is 30 μ m unless otherwise stated.

Figures 3(a)–3(c) compare the phase angle measured for the FOC fabricated using only the PVDF-TrFE-CFE film to that for the FOCs fabricated using the composites of PVDF-TrFE-CFE and fillers MoS₂, rGO, and MWCNT, respectively. Figures 3(b) and 3(c) clearly show that the phase angle level in the 50 kHz–10 MHz range is increased by introducing the conductive fillers rGO and MWCNT into the PVDF-TrFE-CFE films. This could be explained with the overlap of two

FIG. 2. Material characterization of the developed FOC. (a) Cross-sectional SEM image of the MoS₂:PVDF-TrFE-CFE composite. (b) TEM image of the exfoliated MoS₂ nanosheet from MoS₂ bulk powder. The Fourier transform of the image (inset) shows the clear hexagonal symmetry of the thin nanosheet. (c) XRD pattern of PVDF-TrFE-CFE and MoS₂:PVDF-TrFE-CFE composites. (d) Photograph of the flexible/rollable composite and final device.

phenomena. (1) Maxwell-Wagner-Sillars relaxation that occurs at the interface of the filler and polymer matrix. A large difference in the permittivity and conductivity of the filler and the polymer results in the separation of charges at their interface. The interfacial polarization cannot follow the polarity change in the applied voltage; therefore, Maxwell Wagner Sillars relaxation takes place.⁴¹ (2) Dipolar relaxation that takes place at intermediate frequencies due to the lack of the alignment response of the abundant dipoles in the polymer to the polarity change of the applied voltage.⁵ Adding more fillers results in shifting of Maxwell-Wagner-Sillars relaxation towards higher frequencies [Figs. S4–S7]. Therefore, the overlap between the two phenomena increases the phase angle level of the composite at the frequency zone where the dipolar relaxation occurs. This bandwidth, which is termed CPZ earlier in the paper, defines the band of operation frequency for the FOC. If the maximum difference between the measured phase angle and the CPA (computed by averaging the measured phase angle) is set to $\pm 4^\circ$,¹¹ the CPZ becomes 2.5 decades wide between 50 kHz and 10 MHz. This is consistent with the results recently reported in the literature.^{3,46}

The most striking feature of the MoS₂:PVDF-TrFE-CFE composite over the rGO:PVDF-TrFE-CFE and MWCNT:PVDF-TrFE-CFE composites is the formation of a new phase peak on the frequency spectrum in addition to the common two polarization relaxation phase peaks as more MoS₂ fillers are added to the composite. Figure S4(a) shows that this new phase peak is sensitive to the value of f_{MoS_2} . The frequency range where the phase peak takes place also coincides with the phase transition region of MoS₂ as discussed in [supplementary material](#) Sec. S2. This introduces an additional parameter to design the spectrum of the phase angle of the resulting FOC: By changing f_{MoS_2} , locations of three phase angle peaks in the spectrum could be adjusted, which in return affects CPA and CPZ. For instance, for $f_{\text{MoS}_2} = 0.25$, CPA = -58° and CPZ becomes five decades wide between 100 Hz and 10 MHz [Fig. 3(a)] which is the broadest bandwidth reported for an FOC so far.

This concept is extended to other MoS₂-ferroelectric polymer composites to realize FOCs with different CPAs. Figures 4(a), 4(c), and 4(e) plot the phase angle of the FOCs fabricated using PVDF and MoS₂:PVDF with $f_{\text{MoS}_2} = 0.10$,

FIG. 3. Electrical characterization of FOCs fabricated using different composites. The measured phase angle of the FOCs fabricated using (a) MoS₂:PVDF-TrFE-CFE composite, (b) MWCNT:PVDF-TrFE-CFE composite, and (c) rGO:PVDF-TrFE-CFE composite.

FIG. 4. The FOC fabricated using MoS₂:PVDF based ferroelectric polymer composites. The measured phase angle versus frequency and the real part of the impedance Z' versus imaginary part of the impedance Z'' (which are computed using the measured values of the phase angle and the impedance magnitude) (Nyquist plot) for the FOCs fabricated using (a) and (b) PVDF polymer and MoS₂:PVDF composite, (c) and (d) PVDF-TrFE and MoS₂:PVDF-TrFE composite, and (e) and (f) PVDF-TrFE-CFE polymer and MoS₂:PVDF-TrFE-CFE composite.

polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE) and MoS₂:PVDF-TrFE with $f_{\text{MoS}_2} = 0.15$, and PVDF-TrFE-CFE and MoS₂:PVDF-TrFE-CFE with $f_{\text{MoS}_2} = 0.25$ films versus frequency. As reported,⁵ the phase angle peaks different from -90° are observed at 150 kHz–10 MHz due to the dipolar polarization of permanent dipoles in ferroelectric polymers. Inclusion of MoS₂ in the composites slightly increases their CPA values to -80.6° , -70.3° , and -58° from -82.64° , -76.34° , and -64.58° for PVDF, PVDF-TrFE, and PVDF-TrFE-CFE, respectively. The relationship between real and imaginary parts of the impedance (Nyquist plot) of the FOCs fabricated using polymers and composites is provided in Figs. 4(b), 4(d), and 4(f). Here, it is important to note that the nonlinear relationship between real and imaginary parts of impedances in polymers becomes linear in composites (supplementary material Sec. S4). The slopes of these linear relations in Figs. 4(b), 4(d), and 4(f) are 4.90, 2.40, and 1.69 and they correspond to the CPA values of -78.6° , -69.1° , and -59.3° for MoS₂:PVDF, MoS₂:PVDF-TrFE, and MoS₂:PVDF-TrFE-CFE, respectively. These values are in agreement with the CPA values obtained by averaging [Figs. 4(a), 4(c), and 4(e)].

Next, the performances of the FOCs fabricated in this work are compared to those of the previously developed single-component FOCs. Table I clearly shows that the FOCs fabricated using the MoS₂-ferroelectric composites outperform all of the other FOCs when it comes to the bandwidth of the CPZ (see also, supplementary material Fig. S7). It is important to mention here that, previously developed FOCs do not only suffer from narrow CPZs but also have other shortcomings that limit their use in modern electronic devices and systems. For instance, liquid electrode based

(LEB) FOCs cannot be integrated with microelectronics,⁶ the CPA of fractal tree (FT) FOCs cannot be tuned,¹¹ the FOCs making use of operational trans-conductance amplifiers (OTAs) are power hungry,^{47–49} and the CPA of the FOCs fabricated using carbon-ferroelectric polymer composites is very sensitive to the filler ratio of the carbon^{1,3} and it has a low dynamic range.⁴⁶ On the other hand, the FOCs proposed in this work are fully compatible with PCBs, passive, and have a stable CPA over a broader frequency range.

In conclusion, it is shown in this work that a class of FOCs that are fabricated using MoS₂-PVDF ferroelectric polymer composites exhibits a tunable but stable CPA over a broad CPZ. The MoS₂ nanosheets, which are used as fillers in polymers, are exfoliated from a bulk MoS₂ powder by breaking van der Waals forces between layers. The cross-sectional SEM image shows that the exfoliated MoS₂

TABLE I. A comparison of the performances of the single-component FOCs.

FOC type	Constant phase angle (deg)	Constant phase zone (Hz)
FT ¹¹	$-36, -45$	$3 \times 10^3 - 1 \times 10^6$ (2.5 decades)
LEB ⁶	$-5, -15$	$9 \times 10^3 - 3 \times 10^5$ (1.5 decades)
rGO-polymer composite ³	$-30, -67$	$5 \times 10^4 - 2 \times 10^6$ (1.6 decades)
MWCNT-epoxy composite ¹	$-45, -85$	$2 \times 10^5 - 2 \times 10^7$ (2.0 decades)
Ferroelectric polymer ⁵	$-65, -83$	$1 \times 10^5 - 1 \times 10^7$ (2.0 decades)
Ferroelectric polymer layer ⁴⁶	$-65, -83$	$1.5 \times 10^5 - 1 \times 10^7$ (1.8 decades)
CMOS-based emulator ⁴⁹	$-20, -75$	$1 \times 10^1 - 1 \times 10^3$ (2.0 decades)
MWCNT-polymer composite ³⁰	$-7, -65$	$1.5 \times 10^5 - 2 \times 10^6$ (1.1 decades)
MoS ₂ -ferroelectric polymer composite (This work)	$-58, -80$	$1 \times 10^2 - 1 \times 10^7$ (5.0 decades)

nanosheets are distributed uniformly inside the polymer without any aggregation. Furthermore, the structural composition of the composite is investigated using XRD, which confirms that no additional complex molecular structures are generated. The CPA of the fabricated FOCs remains constant between 100 Hz and 10 MHz with a variation of only $\pm 4^\circ$. This CPZ, which is five-decades wide, is not only the broadest among those of the FOCs fabricated using composite films but also the broadest among those of any single-component FOC that has been fabricated so far. All in all, this study demonstrates that a large family of semiconductors can be used to fabricate FOCs that outperform those which have been reported so far in the literature.

See [supplementary material](#) for details.

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- ¹D. A. John, S. Banarjee, G. W. Bohanan, and K. Biswas, *Appl. Phys. Lett.* **110**(16), 163504 (2017).
- ²S. H. Weinberg, *PLoS One* **10**(5), e0126629 (2015).
- ³A. M. Elshurafa, M. N. Almadhoun, K. N. Salama, and H. N. Alshareef, *Appl. Phys. Lett.* **102**(23), 232901 (2013).
- ⁴A. S. Elwakil, *IEEE Circuits Syst. Mag.* **10**(4), 40 (2010).
- ⁵A. Agambayev, S. Patole, M. Farhat, A. Elwakil, H. Bagci, and K. N. Salama, *ChemElectroChem* **4**(11), 2807 (2017).
- ⁶M. S. Krishna, S. Das, K. Biswas, and B. Goswami, *IEEE Trans. Electron Devices* **58**(11), 4067 (2011).
- ⁷G. W. Bohannon, *J. Vib. Control* **14**(9-10), 1487 (2008).
- ⁸A. Potapov, P. Ushakov, and A. K. Gil'mutdinov, *Phys. Wave Phenom.* **18**(2), 119 (2010).
- ⁹A. K. Gil'mutdinov, P. A. Ushakov, and R. El-Khazali, *Analog Integrated Circuits Signal Process* (Springer, Cham, 2017), p. 93.
- ¹⁰A. Kartci, A. Agambayev, N. Herencsar, and K. N. Salama, *IEEE Access* **6**, 10933 (2018).
- ¹¹T. C. Haba, G. Ablart, T. Camps, and F. Olivie, *Chaos, Solitons Fractals* **24**(2), 479 (2005).
- ¹²A. G. Radwan, A. M. Soliman, and A. S. Elwakil, *J. Circuits Syst. Comput.* **17**(1), 55 (2008).
- ¹³A. Adhikary, S. Sen, and K. Biswas, *IEEE Trans. Circuits Syst. I* **63**(8), 1142 (2016).
- ¹⁴A. Elwakil, A. Agambayev, A. Allagui, and K. N. Salama, *Chaos, Solitons Fractals* **96**, 160 (2017).
- ¹⁵L. A. Said, A. G. Radwan, A. H. Madian, and A. M. Soliman, *J. Circuits Syst. Comput.* **26**(10), 1750160 (2017).
- ¹⁶N. A. Z. R-Smith, A. Kartci, and L. Brančík, *J. Circuits Syst. Comput.* **27**(11), 1850172 (2018).
- ¹⁷T. J. Freeborn, B. Maundy, and A. S. Elwakil, *Mater. Renewable Sustainable Energy* **4**(3), 9 (2015).
- ¹⁸A. Allagui, A. S. Elwakil, B. J. Maundy, and T. J. Freeborn, *ChemElectroChem* **3**(9), 1429 (2016).
- ¹⁹T. J. Freeborn, B. Maundy, and A. S. Elwakil, *IEEE Trans. Emerging Sel. Top. Circuits Syst.* **3**(3), 367 (2013).
- ²⁰L. Hu, Y. Ren, H. Yang, and Q. Xu, *ACS Appl. Mater. Interfaces* **6**(16), 14644 (2014).
- ²¹B. Put, P. M. Vereecken, J. Meersschaut, A. Sepúlveda, and A. Stesmans, *ACS Appl. Mater. Interfaces* **8**(11), 7060 (2016).
- ²²A. Shamim, A. G. Radwan, and K. N. Salama, *IEEE Microwave Wireless Compon. Lett.* **21**(3), 117 (2011).
- ²³M. C. Tripathy, D. Mondal, K. Biswas, and S. Sen, *Int. J. Circuit Theory Appl.* **43**(6), 776 (2015).
- ²⁴I. Podlubny, I. Petrás, B. M. Vinagre, P. O'leary, and L. Dorčák, *Nonlinear Dyn.* **29**(1), 281 (2002).
- ²⁵V. Uchaikin, R. Sibatov, and D. Uchaikin, *Phys. Scr.* **2009**(T136), 014002.
- ²⁶R. R. Nigmatullin, *Phys. Status Solidi B* **124**(1), 389 (1984).
- ²⁷G. Carlson and C. Halijak, *IEEE Trans. Circuits Syst.* **11**(2), 210 (1964).
- ²⁸J. Valsa and J. Vlach, *Int. J. Circuit Theory Appl.* **41**(1), 59 (2013).
- ²⁹A. Oustaloup, F. Levron, B. Mathieu, and F. M. Nanot, *IEEE Trans. Circuits Syst. I* **47**(1), 25 (2000).
- ³⁰A. Agambayev, K. H. Rajab, A. H. Hassan, M. Farhat, H. Bagci, and K. N. Salama, *J. Phys. D: Appl. Phys.* **51**(6), 065602 (2018).
- ³¹K. Moaddy, A. G. Radwan, K. N. Salama, S. Momani, and I. Hashim, *Comput. Math. Appl.* **64**(10), 3329 (2012).
- ³²Y. F. Pu, Z. Yi, and J. L. Zhou, *Int. J. Neural Syst.* **27**(4), 1750003 (2017).
- ³³Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* **7**(11), 699 (2012).
- ³⁴F. Purcell-Milton, R. McKenna, L. Brennan, C. P. Cullen, L. Guillemeney, N. Teplakov, A. S. Baimuratov, I. D. Rukhlenko, T. S. Perova, and G. S. Duesberg, *ACS Nano* **12**(2), 954 (2018).
- ³⁵J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, and I. V. Shvets, *Science* **331**(6017), 568 (2011).
- ³⁶W. Lv, H. Wang, L. Jia, X. Tang, C. Lin, L. Yuwen, L. Wang, W. Huang, and R. Chen, *ACS Appl. Mater. Interfaces* **10**(7), 6552 (2018).
- ³⁷M. Zhang, R. C. Howe, R. I. Woodward, E. J. Kelleher, F. Torrisi, G. Hu, S. V. Popov, J. R. Taylor, and T. Hasan, *Nano Res.* **8**(5), 1522 (2015).
- ³⁸C. Wu, T. W. Kim, J. H. Park, H. An, J. Shao, X. Chen, and Z. L. Wang, *ACS Nano* **11**(8), 8356 (2017).
- ³⁹B. Li, S. Zu, J. Zhou, Q. Jiang, B. Du, H. Shan, Y. Luo, Z. Liu, X. Zhu, and Z. Fang, *ACS Nano* **11**(10), 9720 (2017).
- ⁴⁰S. Lee, Y. K. Kim, J.-Y. Hong, and J. Jang, *ACS Appl. Mater. Interfaces* **8**(36), 24221 (2016).
- ⁴¹G. Zhang, D. Brannum, D. Dong, L. Tang, E. Allahyarov, S. Tang, K. Kodweis, J. L. Lee, and L. Zhu, *Chem. Mater.* **28**(13), 4646 (2016).
- ⁴²L. A. Fredin, Z. Li, M. T. Lanagan, M. A. Ratner, and T. J. Marks, *ACS Nano* **7**(1), 396 (2013).
- ⁴³C. R. Ryder, J. D. Wood, S. A. Wells, and M. C. Hersam, *ACS Nano* **10**(4), 3900 (2016).
- ⁴⁴R. Nigmatullin and Y. E. Ryabov, *Phys. Solid State* **39**(1), 87 (1997).
- ⁴⁵K. Zhou, S. Jiang, C. Bao, L. Song, B. Wang, G. Tang, Y. Hu, and Z. Gui, *RSC Adv.* **2**(31), 11695 (2012).
- ⁴⁶A. Agambayev, S. Patole, H. Bagci, and K. N. Salama, *AIP Adv.* **7**(9), 095202 (2017).
- ⁴⁷G. Tsirimokou, C. Psychalinos, and A. S. Elwakil, *Analog Integr. Circuits Signal Process.* **85**(3), 413 (2015).
- ⁴⁸G. Tsirimokou, A. Kartci, J. Koton, N. Herencsar, and C. Psychalinos, *J. Circuits Syst. Comput.* **27**(11), 1850170 (2018).
- ⁴⁹G. Tsirimokou, C. Psychalinos, A. S. Elwakil, and K. N. Salama, *IEEE Trans. Circuits Syst. II* **65**(2), 166 (2018).