Emergence of In-Materio Intelligence from an Incidental Structure of a Single-Walled Carbon Nanotube–Porphyrin Polyoxometalate Random Network

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1. Introduction

Conventional von Neumann architecture, apart from being an arithmetic and logical toolbox, is also transpiring as machine intelligent systems. Complex neural network (NN) algorithms are constantly being designed, updated, and implemented in these devices to accomplish brain-like prediction and classification tasks. This accomplishment of big data handling has its origin in the miniaturization and performance evolution of complementary metal-oxide semiconductor (CMOS) processors consistent with Moore’s law. However, owing to the bottleneck of separate memory and processing units, along with the high fabrication cost associated with device downsizing, unconventional computing with these existing devices is both time and energy consuming. To address this issue, “beyond CMOS technologies” have been emerging at the forefront as “more-than-Moore” devices.[1] Thus, artificial platforms analogous to brain-like information processing and memory operations[2] are now becoming a reality with devices based on nonlinear dynamics.[3–5] High-dimensional nonlinear information obtained as a function of current or voltage output can be treated equivalent to the information generated from software-designed NN architectures when operated by nonlinear activation functions. As such, the only algorithm implementation can be reduced to the training of these current/voltage outputs without the need of a separately designed information processing unit. Thus, unlike their von Neumann counterparts, the hardware implementations can instead pave the way for efficient machine intelligence.
computing. Many such hardware-implemented NN models are being researched\cite{6,7}, however, the one that has recently been attracting attention is directed towards the use of reservoir computing (RC)\cite{8-11} (Figure S1, Supporting Information) because of its bio-inspired and straightforward framework for processing time-series data. Execution of such temporal RC machine has been accomplished in atomic switch networks (ASNs)\cite{12}, conductive polymer network\cite{13}, carbon nanotube (CNT)/polymer composites\cite{14,15}, optoelectrical systems\cite{16,17}, soft bodies\cite{18,19}, spintronics\cite{20,21}, and water tank systems\cite{22}. The productivity of each of these materials towards RC relies on their intrinsic reservoir property\cite{10,11} of recurrent nonlinear high-dimensional dynamics analogous to the human brain\cite{23}. Hence, irrespective of the diversity of their constituent materials and methods of fabrication, the inherent dynamical complexity of these systems facilitates the input-driven computation of RC tasks with only readout weight trainability. Among the many physical systems, ASN- and CNT-based RC offer a resemblance to the brain-like physicality as their solution processible random network integration holds a promising future for large-scale bio-inspired computation. Therefore, materials with these dynamics and physical architectures are constantly being explored. In fact, an example we recently reported is a material that constitutes a system of random networks of single-walled carbon nanotubes (SWNTs) and polyoxometalate (PMO$_{12}$) molecules\cite{24}. The SWNT/PMO$_{12}$ complex imparts nonlinear negative differential resistance (NDR) dynamics at room temperature, signature to the PMO$_{12}$ redox property. The dynamics are a source of noise fluctuations\cite{25,26} and closely resemble the neuronal information processing behavior of the human brain\cite{27,28}. The research showed that by simulating the random network structure of SWNT/PMO$_{12}$, multiple nonlinear fluctuating readouts could be weighted linearly combined to fit a 10th step time-series target function, by training only the readout weights with a regression model, thus successfully implementing the Nonlinear Autoregressive Moving Average (NARMA) task via the RC approach. Based on this concept, in the study presented in this paper we generate a heterotic RC system, where a thin film of SWNT/organic functionalyzed porphyrin-polyoxometalate $\text{SV}_2\text{W}_{10}\text{O}_{40}[\text{H}_4\text{TPP}]$\cite{29} integrated with a microelectrode array (MEA) was used as the in-materio reservoir, while a PC with a regression algorithm was used as the software component. The hybrid system allows us to exploit the intrinsic dynamics of the material to obtain high-dimensional voltage information and directly interface with the software to train and construct various target functions, thereby accomplishing the desired RC-based benchmark tasks (Experimental Section, Figure S2a–c, Supporting Information). The Por–POM is a 3D Keggin-type molecule known to form stable thin films with the characteristic feature of nonlinear NDR behavior\cite{29,30}. However, dynamics such as these have never been exploited towards in-materio machine intelligence applications experimentally. To achieve this, we commenced by forming a reservoir layer of Por–POM with SWNT conductive interconnects, which made it possible to form a random network of SWNT/Por–POM film via a simple sonication method, synchronous to the previous structure\cite{24}. We first discuss the SWNT/Por–POM dynamics via current–voltage ($I–V$) and time–domain current ($I–t$) studies under the influence of DC bias input. The results reflect on the spatio-temporal dynamics manifesting in a source of $1/f^\gamma$ noise useful for brain-like computational performance\cite{28}. The overall network behavior of the device towards sine wave input is also analyzed via Lissajous plots (LPs). Electrochemical impedance spectroscopy (EIS) studies enable a more in-depth interpretation of the LPs, which revealed the emergence of NDR and PSD behavior. High dimensional input information in terms of amplitude, phase, and frequency as readouts allowed the waveform generation RC benchmark task to be successfully achieved with a maximum accuracy of 99.4%. Finally, the in-materio RC functionality towards one-hot target vector binary object classification with Toyota Human Support Robot (HSR)\cite{31} tactile sensing input data was also evaluated. ANN architecture is commonly used to perform classification by utilizing visual information\cite{32,33}, but their occasional faulty outcomes in a low light environment limits their application to fruitful “pick-and-place” operations. Thus, switching to tactile-based data processing via in-materio RC-based learning could prove to be beneficial. In this regard, we exploited the high-dimensional voltage output response of the SWNT/Por–POM and indeed show that the classification becomes more pronounced for readouts of maximized information, contained in the $1/f^\gamma$ power law, thereby leading to the successful accomplishment of supervised one-hot vector binary object classification.

2. Results and Discussion

2.1. SWNT/Por–POM Dynamics and Lissajous Plots

2.1.1. Nonlinear Spatio-Temporal Information Processing

Por–POM with an average unit cell parameter of 2.2 nm\cite{29} was sonicated in combination with SWNT (see Experimental Section) to obtain the SWNT/Por–POM dispersion, as confirmed by the AFM image in Figure 1a. An exposed area of an SWNT with a thickness of 3.2 nm (marked A, Figure S3a, Supporting Information) is increased to 5.4–6.7 nm (marked B and C, Figure S3b,c, Supporting Information) in the presence of Por–POM nanoparticles to provide heterogeneous functionalization driven by sonication. The dispersion was deposited on the MEA (Experimental Section and Figure S2b,c, Supporting Information), and the current dynamics on the sweeping voltage ($I–V$, Experimental Section) were analyzed as shown in Figure 1b. A clear nonlinear increase in the current is observed on both the upward (black line) and downward (red line) scans, followed by a decrease at higher biases of 0.9 and −0.83 V (inset), characteristic of negative differential resistance (NDR) behavior. Molecules of Por–POM are redox active species\cite{30} and have been shown to exhibit nonlinear NDR current behavior under an external bias\cite{29} owing to their charge transfer redox mediated capacitive nature. Along with spatial information, a material intended for use in RC should utilize its nonlinearity to additionally generate useful temporal information when perturbed by an external bias. To examine this, the time-dependent current dynamics ($I–t$, Experimental Section) were assessed under a constant DC input bias of 1 V. As shown in Figure 1c, the $I_{out}$ response against observation window-lengths of 1 s (top), 5 s (middle), and 10 s (bottom), all show noise fluctuations. To qualitatively infer...
the noise information generated from SWNT/Por–POM, we converted the temporal signal of 1 s (top), 5 s (middle), and 10 s (bottom) to the frequency domain and analyzed the power spectral density (PSD, Experimental Section) as presented in Figure 1d. The logarithmic PSD when fitted with Equation (1a) (Experimental Section), followed a $1/f^\gamma$ power law scaling with a scaling factor $\gamma$ of 0.9 (1 s), 1.2 (5 s), and 1.3 (10 s), suggesting that these fluctuations are characteristic of the flicker noise.$^{[34]}$

To confirm that this noise is present in the SWNT/Por–POM device, a similar study of the output response resulting from a 0 V input bias (Figure S4a, Supporting Information) was conducted. Compared with 1 V input, the PSD of 0 V input (Figure S4b, Supporting Information) produces a flat spectrum with a $\gamma$-value of 0.04 and is characteristic of the white noise emergent mainly from the passive components of the DAQ system. The results indicated that the dynamics of SWNT/Por–POM do indeed play an important role in converting the low information white noise to distinguishable frequency

Figure 1. Surface topology with input–output current–voltage and current–time characteristics of SWNT/Por–POM complex. a) AFM image with the height color bar of a single SWNT/Por–POM complex. The exposed SWNT region marked A shows a height of 3.2 nm while the regions marked B and C show the heterogeneous size distribution of 5.4–6.7 nm Por–POM nanoparticles. The values were obtained by measuring the profile shown in Figure S3, Supporting Information. b) Current trace ($I_{\text{out}}$) over cyclic voltage sweeps ($V_{\text{in}}$) with upward (black line) and downward (red line) scan direction. An NDR region is visible for the positive bias at $\approx 0.9$ V. The inset shows the magnified downward bias black encircled region with a similar NDR peak originating at $\approx -0.83$ V. c) Output current response $I_{\text{out}}$ over time when perturbed by a constant DC voltage bias. The responses plotted shows the 1 s (top), 5 s (middle), and 10 s (bottom) observation window-lengths taken from a single-shot experiment of 300 s at 1 V. Fluctuations are present over all the timescales in the current output response. d) The corresponding power spectral density (PSD) plot (black line) against the frequency axis. Each of the PSD corresponds to the window-lengths of the $I_{\text{out}}$ in (c) as depicted by the arrows and is obtained from Fast Fourier Transformation (FFT). The fitting (red line) is done using a power law equation (Experimental Section) through which the scaling factor $\gamma$ was obtained.
information of variable power amplitudes, making it a suitable reservoir material for generating high-dimensional spatio-temporal information. Here, it is worth noting that such spatio-temporal dynamics in the current and PSD are also a signature of other SWNT/polynoroxometalate complexes, in which the contribution from the network-wide redox dynamics was deemed an important parameter for the above findings as conceived by the cellular automata model (CAM) [24,35]. By simulating the random network of SWNT/POM they were able to prove that the material exhibited neuronal correlated activities resembling those of the human brain.[28,36-37] The model clearly suggests that perturbation by an external increasing bias enabled a network-wide cascade of charge-discharge processes at different timescales owing to the multiple redox states of the POM molecules. As SWNT/POM capacitive junctions of varying potential gradients are possible, noise fluctuations in the current output are obvious, thereby rendering random fluctuations of nonlinear NDR dynamics along with $1/f^\gamma$ of maximized information, a signature for brain-like “edge of chaos” computation.[38,39] To validate the theoretical concept derived from CAM, we also speculated about the nature of PSD for varying bias as shown in Figure S4c, Supporting Information. As before, relative to 0 V input, the PSD of each bias input in Figure S4d, Supporting Information, showed similar $1/f^\gamma$ character, where the $\gamma$ factor changed abruptly with the increasing input bias (Figure S5a, Supporting Information). To understand this behavior, we also plotted the change in noise amplitude $A$ (Equation (1a), Experimental Section) against the input biases, as shown in Figure S5b, Supporting Information. The magnitude of $A$ in $1/f^\gamma$ noise plays a significant role in supporting the redox mediated dynamics as it has been correlated to the free charge carriers available for conduction in the material and is found to be inversely proportional to it.[40] Usually, whenever the bias changes, the Por–POM molecules undergo a redox state change in which either the free carriers are discharged or the Por–POM is charged. Generally, when $A$ decreases, free carriers can be discharged throughout the network. This gives rise to an increase in current, but when the opposite happens, more free carriers are taken up by the Por–POM to be charged, leading to low current response and high noise output, as schematically presented in Figure S5c,d, Supporting Information. Our variable $A$ with bias change supports the CAM derived noise fluctuation arising from POM redox and we believe that it is this transition of noise amplitude at different bias voltages that leads to the observed nonlinear current increase with NDR dynamics in $I$–$V$ (Figure 1b) and a variable $\gamma$-value for the slope in the PSD. It should also be noted from Figure 1d, that these fluctuations in the current satisfy the condition of $0 < \gamma < 2$ for any observation window-length and support the scale-free nature of the events.[41] This is a signature of the $1/f^\gamma$ power law, which suggests that the information generated from the input is solely an intrinsic property of the material and hence is retained over all lengths of the processing time.

2.1.2. High-Dimensional Reservoir States—Lissajous Plots

Apart from the nonlinearity and spatio-temporal information processing ability, a reservoir should also generate multiple dynamics from within the network to aid with the reservoir task of prediction or classification. To reflect on this aspect of rich reservoir states, the network-wide I/O response from SWNT (black line)/Por–POM (green circles) was assessed with a time-varying sine wave input using custom-built equipment (Figure S2a, Supporting Information). Figure 2a schematically shows the measurements where a sine wave of 11 Hz and $\pm 1$ V was provided as the input ($V_{in}$) to one electrode pad (yellow) while voltage readouts ($V_{out}$) from the other electrode pads, grounded via the DAQ, were collected and investigated on the basis of the Lissajous plots (LPs)[42,43] ($V_{in}$ vs $V_{out}$) in more detail. A multitude of LPs, color-coordinated with the output electrode pads in Figure 2a, can be seen in Figure 2b–e. Figure 2b,c shows the slightly nonlinear (in the input voltage window of $\sim 0.16$ V to 0.15 V) nature of the output sine wave with attenuated amplitude and is in-phase with the input (Figure S6a–c, Supporting Information). Upon further examination, LP profiles in the form of a distorted ellipse (Figure 2d) and with hysteresis behavior (Figure 2e) were also obtained. In these cases, the decrease in amplitude is relatively high and is accompanied by multiple NDR-like fluctuations with a large amount of hysteresis, which is indicative of phase-delayed outputs (Figure S6d,e, Supporting Information). Along with these spatial entities observed for AC, temporal information in terms of frequencies is also realized where the fundamental input sine wave frequency decomposes into higher harmonic generations (HHG) from each of the output electrode pads (Figure S7, Supporting Information). These profiles indicate that the random network creates pathways of complex junctions at each of the electrode pads and with the intrinsic nonlinearity it encodes the input signal into higher dimensional spatio-temporal outputs. To interpret this analogy, we used electrochemical impedance spectroscopy (EIS) (Experimental Section, Figure S8 and S9, Supporting Information). The Nyquist plots (Figure S8a–e, Supporting Information) of the pads colored green and black (Figure 2a) show a well-defined semicircle at high frequencies (to the left of the x-axis), but as we moved closer to the low-frequency regime (to the right of the x-axis), a distortion is observed. We find this behavior to be coincident with the $I$–$V$ plot at a higher scan rate in Figure S8f, Supporting Information, where it showed no fluctuations as compared with the lower scan rate in Figure 1b. On the other hand, the Nyquist plots for the pads colored red and blue (Figure 2a) show a very abrupt and noisy impedance change overall except for the regions close to the high-frequency region (1 MHz) (Figure S9a–f, Supporting Information). Both these results correspond well with the nature of the LP we obtained before strengthening the fact of having multiple complex junctions within the network. To analyze this, we fitted the Nyquist plots in Figure S8, Supporting Information, and found that the equivalent circuit consists of two resistor–capacitor elements corresponding to grain interiors and electrode interfaces, similar to the previous study.[29] The extracted values of the resistance and capacitance (Figure S10a, Supporting Information) shows a clear magnitude difference thereby emphasizing the role of the random network in creating variable and complex network-wide pathways for producing such rich spatio-temporal information as on the LP and HHG plots. Although a proper fit could not be achieved for those in Figure S9, Supporting Information, we could assume that more complex resistive–capacitive pathways are present at these junctions where the intensity of the
redox behavior is higher than at the other pads. Apart from interpreting the LP, EIS also facilitates an understanding of the dynamics of the system responsible for nonlinear NDR behavior and frequency-dependent PSD. We addressed the first of these problems by measuring the effect of resistance and capacitance as a function of the applied DC bias. We extracted the parameter values after fitting each Nyquist plot and ignored the effect of the grain boundaries because it is negligibly small and continued with the electrode interface components. As we increased the bias, both the quantities were observed to increase nonlinearly, as shown in Figure S10b, Supporting Information. The capacitance is observed to increase, suggesting that with higher bias, a greater amount of charge can be stored in the Por–POM for multiple redox reactions. This gives rise to a lesser flow of free carriers and hence an increase in the noise amplitude, which is in good correspondence with the result in Figure S5, Supporting Information. This also leads to an increase in the resistance even at higher bias thus supporting the observation of decreasing

Figure 2. SWNT/Por–POM complex network-wide dynamics via Lissajous representations. a) Shows the full circuit schematic of the outputs obtained from different electrode pads when a sine wave of 11 Hz, ±1 V is applied at the yellow-colored electrode pad connected to the SWNT (black line)/Por–POM film (green circle). A function generator is used where the output from one pole is fed as the input signal, whereas the other pole is grounded via a 50 Ω resistor (z value, orange box). All outputs are then taken from the DAQ system which too is grounded via a similar 50 Ω resistor, to complete the full circuitry. b) Slightly nonlinear Lissajous plot (LP) with no phase delay shows a proportional change in V_{out} amplitude relative to the V_{in} representative of resistive pathways. c) The nonlinear LP represents the charge–discharge phenomena occurring but with signals in phase with the input. d) The elliptical and the e) hysteresis with NDR like fluctuations show phase delays corresponding to the complex capacitive network pathways. The color of the plots is coordinated with the electrode pads in (a), indicating the outputs showing the same behavior.
current with increasing bias in \( I-V \) (Figure 1b) to fulfill the nonlinear NDR effect. To comply with the nature of the PSD obtained from the DC bias, we considered deriving the voltage power spectral density from the Nyquist theorem given by Equation (1b) (Experimental Section). The logarithmic plot shown in Figure S10c, Supporting Information, closely followed the 1/2 power law behavior coincident with the PSD result obtained using DC bias (Figure 1d). Thus, based on the finding, we can suggest that the heterogeneity along with random network structure creates varying degrees of cascading nonlinear redox activity at different points in the network over the entire time-length, thereby generating pathways of different electrical properties of resistive or capacitive nature. As a result, a mixture of LPs is generated from a single unit of SWNT/Por–POM with high-dimensional information of the input in terms of amplitude, phase, and frequencies. Intrinsic electrical properties of this nature that are nonlinear with network wide high-dimensionality and obey the 1/2 power law of maximized information processing, and are manifested in a recurrently connected random network structure, have recently proven to play a key role in in-materio RC tasks of binary classification and prediction. Thus, by utilizing the innate dynamics emergent from our SWNT/Por–POM reservoir, we proceeded to establish the RC benchmark tasks of waveform generation and object classification, which we present in the next sections.

2.2. Waveform Generation Task

The waveform generation task forms the experimental basis of sine wave Fourier series transformation, and this was demonstrated by adopting the in-materio RC procedure (Figure S11a, Supporting Information). Figure 3 shows the RC task result of waveform generation obtained from 11 electrode readouts (O1 to O11, Figure 2a). Weighted sine wave outputs were initially trained (Figure S11b,c, Supporting Information) and fitted (green curve, Figure 3) with the respective targets of triangular, cosine, square, and sawtooth waveforms (black line, Figure 3). After training, a test waveform was reconstructed (red curve, Figure 3) and its fitting accuracy with the specific target waveforms was assessed to evaluate the effectiveness of the RC training model. A detailed explanation of RC training and testing is provided in the Experimental Section. The triangular test waveform (Figure 3a, red) had the highest test accuracy of 99.4% (red line) after training (green line) followed by cosine (99%, Figure 3b), square (87%, Figure 3c) and sawtooth (71%, Figure 3d) in this decreasing order. To verify whether the target waveforms could be constructed by using any number of electrode readouts, we further evaluated the test fitting accuracy resulting from training a lower number of output weights, as shown in Figure 3e. The test fitting accuracy for constructing the triangular waveform showed that RC delivered highly consistent performance as we successively lowered the number of output pads that were trained from 11 to 3 (Figure S12 and S13, Supporting Information, show the results for seven and three output pads). A slight decrease was however observed when two and one output pads were trained (dashed box, Figure 3e), but the overall accuracy was successfully maintained above 90%. The reason this trend is followed accurately is because, owing to its high resemblance to a sine wave shape, the triangular waveform as such can be easily replicated with the fundamental and lower addition of odd harmonics (Equation (S4), Supporting Information). On the other hand, although the training performance of 11 to 6 output pads (Figure S12, Supporting Information) was observed to be consistent for cosine, sawtooth, and square targets, the test accuracy of the training outputs for fewer than six pads (Figure S13, Supporting Information) was clearly lower (dotted box, Figure 3e), with the maximum change observed for cosine. The result reflects the importance of the correlation of the high-dimensional aspect of the reservoir to the number of electrode outputs. The replication of complex waveforms such as square and sawtooth are well known to require infinite linear combinations of higher harmonic sine waves with varied amplitudes and phases (Equation (S6) and (S7), Supporting Information). In this case, as we tend to use fewer output pads for training, we not only reduce the inclusion of spatio-temporal sine wave outputs (Figure S6, Supporting Information and Figure 2b–e) but also lower the weighted linear terms, hence making it difficult to train or optimize the weights accurately for a closer fitting. The same situation arises for cosine, although it does not require any higher harmonics (Equation (S5), Supporting Information); however, the absence of phase shifted sine wave outputs (Figure S6, Supporting Information and Figure 2b,c) enables their conversion to proper cosine curves. The above result thus emphasizes the fact that for a reservoir to learn different time-series waveform targets efficiently, the presence of multiple linear/nonlinear transformations of the input in terms of amplitude, phase, and frequency is indeed vital. Instead, this input-driven spatio-temporal information contained in each of the readouts represents the contrasting computational regime of reservoir states emerging from the random network of SWNT/Por–POM, hence enabling the network to carry out the machine intelligence task of supervised learning.

2.3. RC-Based Toyota HSR Tactile Sensing Object Classification

The SWNT/Por–POM reservoir was also exploited for another benchmark task of object classification by utilizing tactile sensory input datasets of the Toyota HSR, details of which are provided in the Experimental Section. Briefly, the panel on the left in Figure 4a shows the HSR, with an elaborated schematic of its arm attached to the gripper via a force-torque sensor, as shown on the right. The sensor generates tactile sensory information of the grasped objects by measuring the change in the gripper angle \( \theta \) as a function of the applied forces. Four toys of mixed hardness and softness, namely a bus, block, dog, and hedgehog (HH), were used in this study as depicted from top to bottom in the red box to the right of the schematic in Figure 4a. The raw data gathered during tactile sensing, plotted in Figure 4b on the left, of each of the grasped objects was preprocessed and converted to time-series voltage data using LabVIEW software as shown in Figure 4b on the right. During preprocessing, bits of DC-like input biases of different voltages are produced. These data are used to perturb the SWNT/Por–POM reservoir to fetch high-dimensional spatio-temporal voltage information particular to a given object. These input time-series datasets of the individual...
objects were then fed to the device one at a time, and their corresponding outputs were collected from all the electrode pads, which were finally used for training and testing the binary classification, an example of which is shown in Figure 4c. A supervised regression model, constructed using Python, was adopted to first train with the desired one-hot target vector illustrated in Figure 4d, where the weights of the correctly classified object were optimized to represent the target vector value of “1,” whereas the other objects were optimized to the value “0.” The trained weights for each object were ultimately used for testing the one-hot vector binary classification and once all the test datasets were evaluated, the compiled result was plotted on one graph, as shown in Figure 5. The respective objects, the HH (Figure 5a), Dog (Figure 5b), Block (Figure 5c), and Bus (Figure 5d) were correctly predicted in the presence of the other objects to give a likelihood of vector target value of “1.” It is to be noted that in each of the cases the classification happens after a certain time-step before which it remains unclassified as marked by the colored rectangular box. This can be understood by the extent of information processing arising from

![Figure 3.](image)

**Figure 3.** Training and testing of waveform generation RC task by linear combination of sine wave outputs from SWNT/Pol–POM reservoir when perturbed by a sine wave input of ±1 V and 11 Hz. a) triangular, b) cosine, c) square, and d) sawtooth waveform generation RC task. Eleven output weights of 1 s epoch are first trained via supervised learning (green line), and the performance is evaluated for the next 1 s epoch through the accuracy between the target (black line) and test data (red line). Triangle shows the best fitting with the highest test accuracy followed by cosine, square and sawtooth. e) The graph shows a variation of test accuracy between the target and test data fitting with the number of tested outputs. The yellow dotted box represents the decrease in fitting for all waveforms when lower number of outputs were trained. It suggests the correlation between the requirements of higher dynamics via more output training to get the best RC-based learning.
Compared to "Region A," the nonlinear NDR-like high-dimensional fluctuations are more pronounced in "Region B," which leads to a distinct increase in the scaling factor $\gamma$, as is evident from the PSD plots (Figure S14b–f, Supporting Information) of a certain time section. This characteristic behavior of both of the regions is replicated over the entire time-step as depicted in the short-term Fourier transform (STFT) (Figure S15, Supporting Information). This supports the fact that, similar to waveform prediction, classification tasks also require the maximization of information to correctly optimize the weights via supervised learning to successfully achieve the binary classification task. Here, it is noteworthy that the performance of the in-materio RC device consisting of SWNT/Por–POM for classification, replicates the results of an algorithm-based echo state network (ESN) approach as reported previously.\cite{47} Moreover, the in-materio object classification with a random network of SWNT/Por–POM (Figure S16a,b, Supporting Information) was also
highly efficient with power consumption of $\approx 300 \mu W$ (Figure S16c, Supporting Information for calculation) to compute this task. Thus, the present analysis substantiates the fact that low-dimensional material platforms with their nonlinear information processing capability have the potential to emulate their software analogues to accomplish efficient task performance using machine intelligence. A unified structure consisting of a processing and learning unit can hence emerge as an alternative “in-materio neural network architecture” for the present day von Neumann ones, leading to a paradigm shift in the field of straightforward unconventional computing.

3. Conclusions

In summary, we demonstrated the successful implementation and integration of RC at the hardware level with SWNT/Per–POM as an in-materio RC material integrated with the MEA architecture. The design proves convenient for RC as it allows easy recording of multiple reservoir states from different points of the network via the terminal pads. The functionalization of SWNT with Per–POM transforms it into a suitable reservoir material because the fundamental reservoir property of nonlinear spatio-temporal dynamics can be realized by applying external bias. The $1/f^\gamma$ power law behavior, associated with the correlated cascading of charge–discharge activities, emphasizes the ability of the SWNT/Per–POM to process information at the “edge of chaos” in a way similar to the human brain. This maximization of input information proved beneficial for the RC task of object classification utilizing the Toyota HSR tactile sensory input data. The output responses for each of the four toys of different hardness, a hedgehog, dog, bus, and block, produced a likelihood of vector value “1” in binary classification after training with their respective supervised one-hot vector target. The results replicate the performance delivered by a software-designed ESN remarkably well, indicating the importance of the hardware platform towards implementing RC. Likewise, the RC task consisting of triangular, cosine, square, and sawtooth waveform generation was also accomplished with a minimum fitting error of 0.006. The success behind this lies in the sine wave output responses of varying amplitudes, phase, and higher harmonics relative to the input. Weighted linear combinations of these outputs after supervised learning resulted in the reconstruction of simple to complex waveforms, thereby supporting the ability of the SWNT/Per–POM reservoir to act as a mathematical Fourier transform functional unit. It is indeed crucial to know that such a task also relies on the linear combination of the number of outputs and suggests the use of a larger number of combinations to obtain a lower error rate when fitting complex waveforms. The above results suggest the emergence of in-materio machine intelligence in the SWNT/Per–POM reservoir. Properties such as low-cost
solution processibility, nonlinear NDR-like spatio-temporal dynamics, the 1/f noise power law characteristic of information maximization, and the performance on supervised RC tasks make the low-dimensional molecular network of the SWNT/Port–POM–MEA architecture a desirable platform for in-materio RC. We expect these functional capabilities, along with their potential of large-scale integration on variable substrates in the form of families of different polyoxometalate molecules complexed with SWNT, to pave the way for the development of a closer analogue of bio-inspired unconventional computing in the near future.

4. Experimental Section

Synthesis of SWNT/Port–POM Dispersion: HiPco SWNTs (purchased from NanoIntegris) with an average diameter of 1.2 nm and an average length of 1 μm were purified by annealing at 200 °C, followed by boiling under HCl reflux to remove the amorphous carbon and Fe catalysts. The acid-treated SWNTs were washed with DI water, and dried to collect the purified material. We functionalized the purified SWNTs with Port–POM using ultrasonication.[48] First, the purified SWNTs (2 × 10−2 g L−1) were sonicated in ethanol for 1 h to initialize the unbundling process. We then added Port–POM (4 × 10−2 g L−1) in ethanol to the SWNT dispersion and ultrasonicated it for another 4 h to enhance the unbundling process. The resultant dispersion was centrifuged at 1000 g for 15 min, and the excess supernatant of Port–POM was discarded. The precipitate was again sonicated in ethanol to obtain the final stable dispersion of SWNT/Port–POM.

Fabrication of MEA for RC: An aluminum-coated MEA was patterned onto a borosilicate glass substrate (Figure S2b, Supporting Information). The substrate was cleaned with IPA followed by DI water using a bath sonicator at 28 Hz for 3 min. A lift-off resist, LOR-10A, was then spin-coated onto the substrate with a spin coater at 3000 rpm for 50 s and was dried at 180 °C for 5 min on a hot plate. This was followed by the deposition of the photomask S18186, spin-coated at 4000 rpm for 2 s, and eventually dried on a hot plate at 90 °C for 5 min. The pattern was developed by placing a mask atop the substrate and exposure to UV light for 25 s using a photolithography machine. The resist was developed using MF 319 developer for 90 s, after which it was washed with DI water and baked at 120 °C for 5 min to obtain the desired pattern. A layer of aluminum metal with a thickness of 50 nm was sputtered onto the pattern and the LOR was removed by submersion in dimethyl sulfoxide at 60 °C for 20 min.

Deposition of the SWNT/Port–POM Thin Film: An existing vacuum-assisted wet transfer process[24,49] was adopted to initiate the deposition of the SWNT/Port–POM thin film (Figure S2c). A dispersion of SWNT/Port–POM dispersion (500 μL) was filtered through nitrocellulose filter paper (1 μm mesh, MCE, Millipore) and placed atop the circular pads of the electrode array. A few drops of acetic acid were casted on the filter paper, which left the substrate with only the SWNT/Port–POM film. The sample deposited on the substrate was then placed on top of a glass vial, 80% filled with acetic acid, and was dried by vaporizing the acetic acid by heating the solvent to 80 °C for 30 min.

Characterization and Measurement: Atomic force microscopy (AFM) images of a drop-casted dispersion of SWNT/Port–POM on the Si/SiO2 substrate were acquired using a JEOL JSPM-5200 instrument. The I–V characteristics of the fabricated sample were recorded under a DC sweep bias of ±1 V at a scan rate of 25 mV s−1, utilizing a probe system (Pascal Co., Ltd) with a semiconductor parameter analyzer (Agilent 4156B). The I–V and input–output relations for constructing the Lissajous plots were obtained, and the RC tasks of waveform generation and object classification were completed using a custom-built electrical set-up (Figure S2a, Supporting Information). For I1, a constant DC bias voltage of 1 V for 300 s was supplied via the input electrical probe. The voltage response was converted into current by placing an additional 1 MΩ resistor along with a variable gain low noise current amplifier (DLPCA200) in between the output electric probe and DAQ system. The power spectral density (PSD) was obtained by fast Fourier transformation (FFT) of the respective output response of the I–t measurement. The size of the observation window was varied within the entire window of 300 s and used to plot the results. The logarithmic plots of the PSD were fitted using the power law equation in Equation (1a), where A and y represent the noise amplitude and the scaling factor, respectively. Both the FFT and fitting were conducted using Origin Pro 9 software. The EIS measurements were carried out using a Solatron 1260 instrument with a dielectric interface. Measurements were performed using a ±1 V AC supply by varying the frequency from 0.01 Hz to 1 MHz and the DC bias from 0.0 V to 1.0 V in increments of 0.2 V. The PSD, Figure S10c, Supporting Information, was plotted using the Nyquist theorem given by Equation (1b), where k is the Boltzmann constant, T is the absolute temperature, and z is the real impedance. All the measurements were performed at room temperature (24 °C) and pressure.

\[ \text{Power law} = A f^y \]  
\[ \text{PSD} = 4.4kTz^2 \]  
\[ \frac{W_{out}}{O(t)} = O(t)^{-1}O(Y) \]  
\[ F(t) = \sum w_{out} X_i(t) \]  
\[ \text{NMSE} = \frac{1}{N} \sum \frac{Y_i(t) - O(t)}{Y_i(t)}^2 \]  
\[ \text{Accuracy} = (1 - \text{NMSE}) \times 100\% \]
normalization to produce a value in the interval of $[0, –1]$ V. An input gain of “5” was multiplied with the values throughout to change the interval to $[0, –5]$. These values were then used as input for the device by using the LabVIEW software interface to carry out the desired RC task of classification.

**RC One-Hot Vector Binary Object Classification:** Five time-series voltage datasets $V_m^{in}$ generated by grasping each object $m$ (HH, dog, bus, and block) were used as inputs for the custom-built set-up in Figure S2a, Supporting Information. For each input dataset, a total of 11 voltage readouts, termed $V_m^{out}$, were collected, where $i$ represents a readout from a specific electrode pad. Thus, each input dataset had one output dataset containing a set of 11 voltage readouts, which were all sampled by the DAQ (Figure S2a, Supporting Information) at 1000 points s$^{-1}$. The method was continued for other four input datasets of that particular object and once over, was repeated for the other objects. After gathering all the information from the SWNT/por–POM in-materio reservoir, the classification task was performed off-line using the software integrated PC. Here a supervised machine-learning approach was also adopted with the aim to fit the weighted $(W_{m}^{in})$ linearly combined reservoir output $z^m(t)$, given by Equation (6), to a given one-hot vector target signal (Figure 4d).

The one-hot vector target signals represented the labels of the object $m$ to be predicted, and their lengths were equal to the time length of the input data. The object to be classified correctly needed $z^m(t)$ to be fitted with the vector target value 1 of $y^m(t)$, while all other $z^m(t)$ were fitted to the $y^m(t)$ vector value of 0. Thus, initially, 80% of the output datasets were used for training with the targets and then the remaining 20% were used for testing the classification performance of the device. For training, only the output weights $W_{m}^{out}$ were optimized using a Python-encoded ridge regression model with a ridge regularization coefficient ($\lambda$) value with which the identity matrix $I$ was multiplied, as expressed by Equation (7). Here, $T$ represents the transpose of the voltage output matrix $V$ (bold represents matrix format) constituting all the 11 time-series readouts. Lastly, the trained $W_{m}^{out}$ were then linearly combined with the test datasets using Equation (6) to finally have an inference on the classification ability of the SWNT/por–POM reservoirs.

$$Z(t) = \sum_{m=1}^{11} W_{m}^{in} V_{m}^{out}$$  \hspace{1cm} (6)$$

$$W_{m}^{out} = ((V_{m}^{out})^T V_{m}^{out} + \lambda I)^{-1} V_{m}^{out}$$  \hspace{1cm} (7)$$

**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 in the supplementary material of this article.

**Keywords**

artificial intelligence, object classification, physical reservoirs, recurrent neural network, waveform generation

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