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In-materio computing in random networks of carbon nanotubes complexed with chemically dynamic molecules: a review

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In-materio computing in random networks of carbon nanotubes complexed with chemically dynamic molecules: a review

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Abstract

The need for highly energy-efficient information processing has sparked a new age of material-based computational devices. Among these, random networks (RNWs) of carbon nanotubes (CNTs) complexed with other materials have been extensively investigated owing to their extraordinary characteristics. However, the heterogeneity of CNT research has made it quite challenging to comprehend the necessary features of *in-materio* computing in a RNW of CNTs. Herein, we systematically tackle the topic by reviewing the progress of CNT applications, from the discovery of individual CNT conduction to their recent uses in neuromorphic and unconventional (reservoir) computing. This review catalogues the extraordinary abilities of random CNT networks and their complexes used to conduct nonlinear *in-materio* computing tasks as well as classification tasks that may replace current energy-inefficient systems.

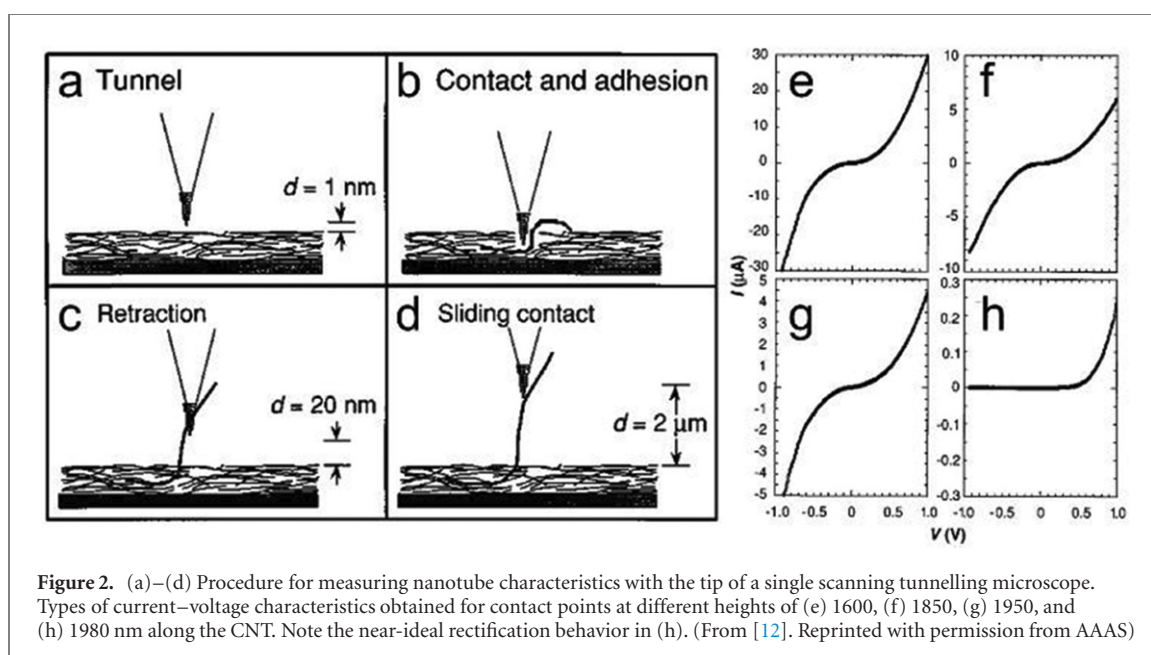
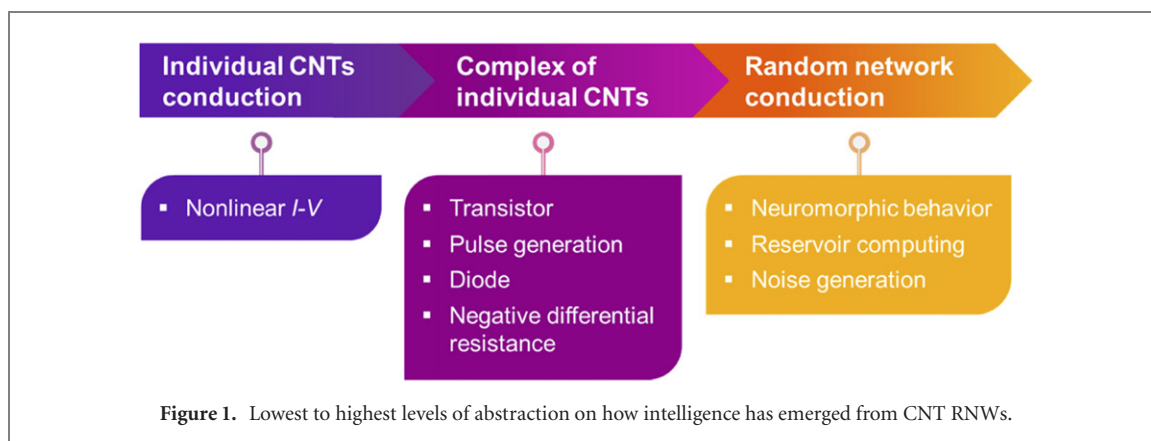
1. Introduction

With the rapid progress of software-based artificial intelligence (AI), the high energy consumption of contemporary complementary metal-oxide-semiconductor (CMOS) systems has become a major concern. Therefore, analog hardware-based AI techniques are required [1]. Notably, innovative analog-based phenomena derived from the material sciences present exciting new opportunities. For example, material-based composites have been found to enable signal processing, computation, and memory storage, which if configured properly, may be from 10 to 100-times more efficient, thus easing energy burdens.

This study contributes to the future development of neuromorphic AI hardware by cataloguing the intelligent capabilities inherent in random networks (RNWs) that combine nonlinearity and other properties [2–8] to mimic the dynamics of the human brain [9, 10]. This review provides a historic review of carbon nanotube (CNT) RNWs and their composites to better understand their conductive and neuromorphic properties, as illustrated in figure 1.

2. Electric nonlinearity of individual CNT and CNT complexed with molecules

At the microscopic scale, the human brain exhibits clearly nonlinear dynamics [9, 11]. To reproduce synaptic and neuromorphic properties, a combination of two nonlinear components (i.e., a CNT and molecule) is essential. For a synapse, the CNT/molecule component should be such that it resembles the nonlinear resistive switching characteristic. Such dynamics give rise to multiple resistive/conductive states, representative of biological synaptic weights, from within the network, hence making it more of a memory unit, where the states can be modified by controlling the charge influx through it via external stimulation. While, for emulating the biological neuron, energy efficient information generation, such as spike interval or density is required from a

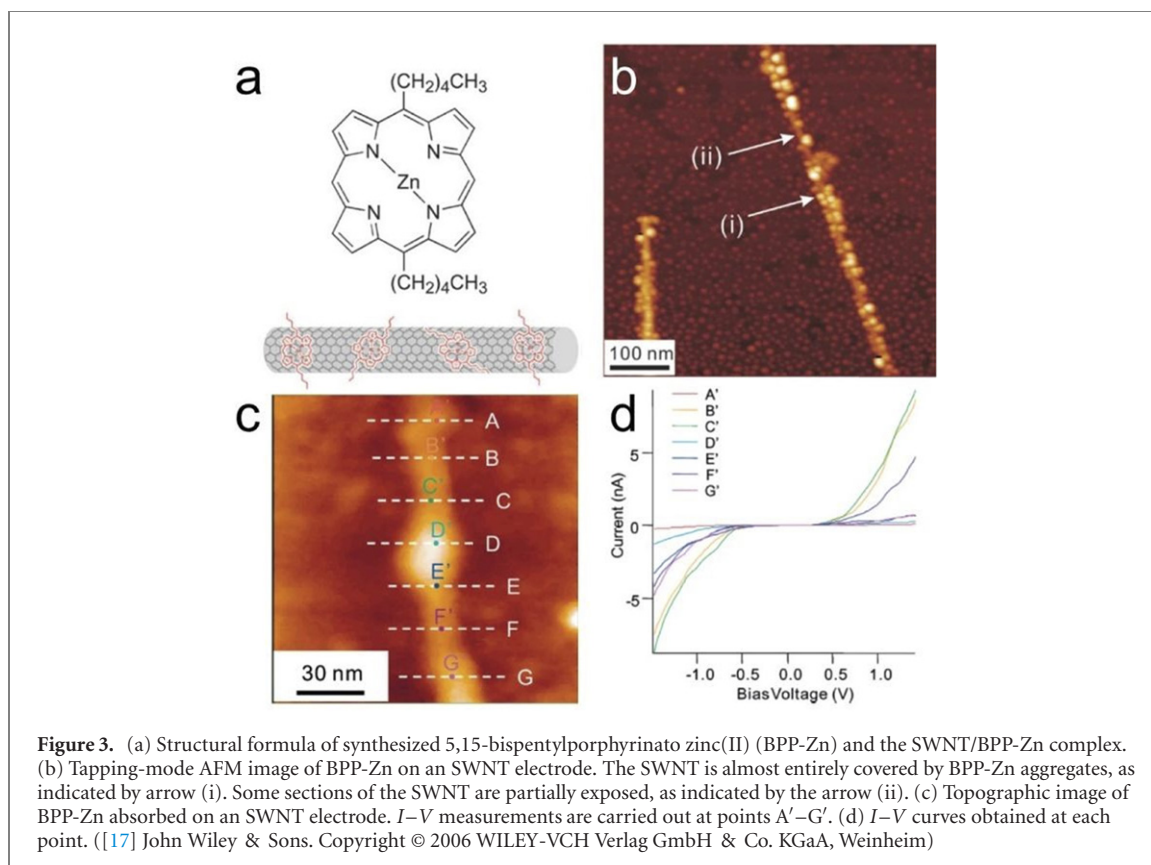


molecular functionalized CNT system. As such, the device dynamics should closely exhibit the negative differential resistance behavior in its current–voltage profile, where, after an initial non-ohmic conductance increase a rapid decrease, under the window of an increasing external stimuli, is followed. Therefore, we now examine nonlinear conduction in CNTs.

Many methods have been reported for measuring CNT electrical properties. However, the measurement of isolated CNTs was not possible until the late 1990s, when the tip of a scanning tunnelling microscope was found to induce induction and voltage (I – V) characteristics (figure 2). It was found that varying the distance between the tip and the substrate and changing CNT lengths created a variety of nonlinear I – V results that are consistent with the localized charge transport mechanism that currently allows the existence of nanoscale electronic devices [12]. Both metallic and non-metallic behaviors have been observed, along with abrupt jumps in conductivity via temperature variances [13]. This report is the earliest case of CNTs having been confirmed to exhibit nonlinear conduction without substrate interference.

Nonlinear conduction in field-effect transistors (FETs) has also been investigated. In 1998, an FET based on isolated semiconducting CNTs was fabricated and electrically measured using gate bias voltage to alter the shape of the source-drain I – V curve [14]. Tunnelling thin-film transistors (TFTs) have also emerged as potential candidates for replacing low-voltage CMOS FETs. A triple-gate CNT TFT FET, fabricated by introducing a sharp n–i–p doping profile via electrostatic doping, demonstrated a subthreshold swing (SS) of sub-60 mV/decade in a band-to-band tunnelling operation. The operation mechanism was found to overcome the fundamental SS limit of 60 mV/decade at room temperature. The nonlinear output characteristics observed in TFET operations indicate that one-dimensional CNTs are the optimal channel material for overcoming drain-induced barrier thinning by operating within the quantum capacitance limit [15].

Some nanoparticle (NP)-based CNT complexes have been found to show specific electrical properties from the combination of CNTs and adsorbed NP molecules [16]. One approach for obtaining electrical nonlinearity

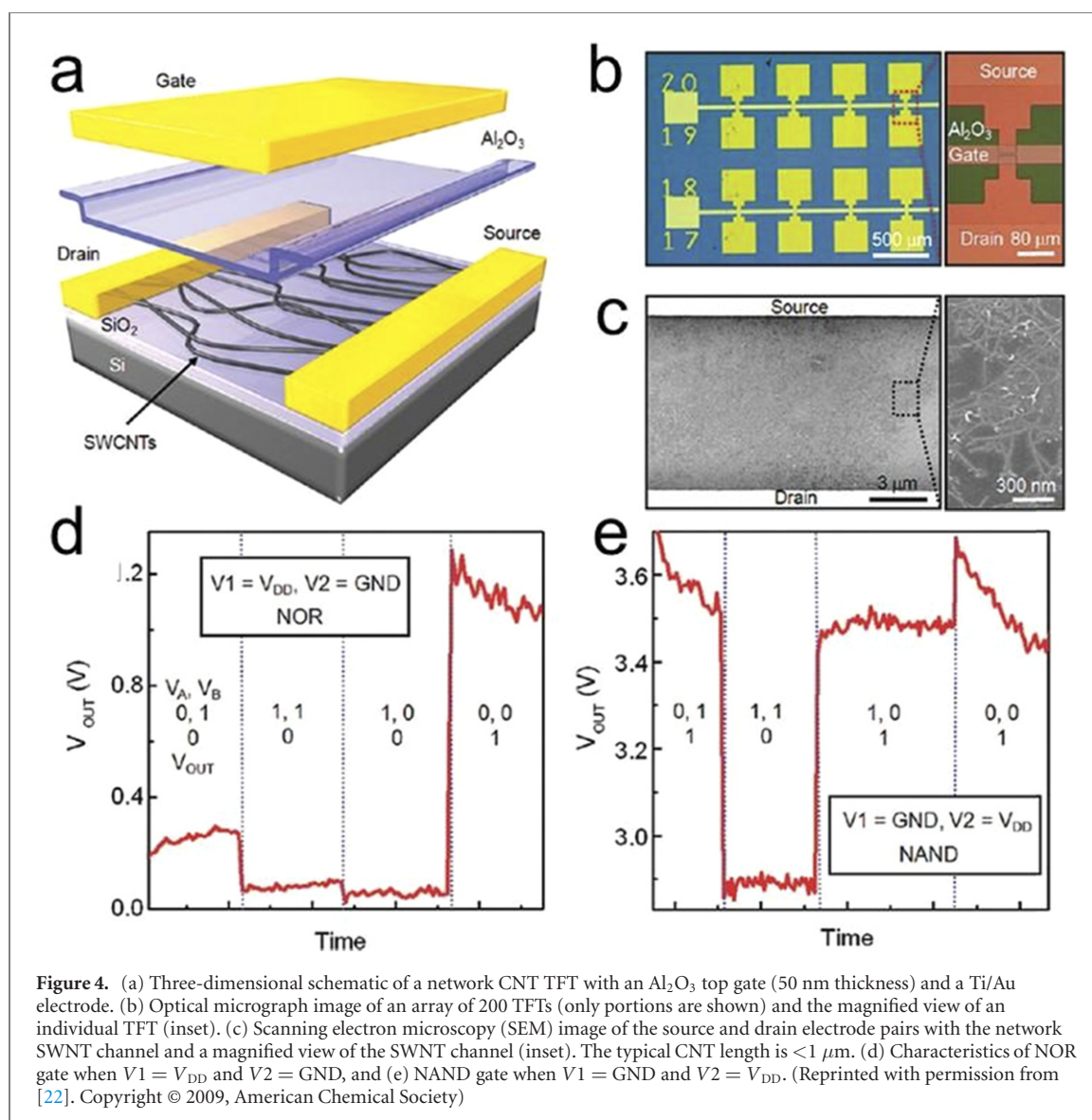


is to complement NP materials with CNTs for electrical functionalization. Many types of materials have been reported to support this. For instance, Tanaka *et al* reported the adsorption of 5,15-bis(pentyl)porphyrinato zinc(II) (BPP-Zn) NPs on the sidewalls of single-walled nanotubes for electrical functionalization, as shown in figures 3(a) and (b). Point contact current imaging atomic force microscopy (AFM) was used to measure the $I-V$ curves, which showed nonlinear electrical properties as a result of the NPs behaving as nanodiodes on the single-wall nanotube (SWNT) wiring [17]. Another report suggested that a porphyrin single molecule can operate as a point local gate for individual SWNT FETs owing to the redox of a single molecule [18], which can be a source of telegraph noise of the system.

Similar studies using a 150mer-porphyrin polymer (150mer-porph) also reported enhanced conductivity of SWNTs owing to the π electron donation from the 150mer-porph [19]. Conductivity measurements with metallic nanotubes isolated from pristine SWNTs showed that SWNTs become semiconducting in the presence of metal NPs [20]. This was further expanded to SWNT-adsorbed phosphomolybdic acid ($\text{PMO}_{12}\text{O}^{-40}$; POM), which results in an SWNT/POM junction in which rectification direction inversion arises from SWNT particle size or chirality. Kelvin probe force microscopy measurements showed that the charge distribution of POM/semiconducting SWNTs was opposite to that of POM/metallic SWNTs [21].

Other CNT-based CMOS approaches exist. For example, a CMOS-like inverter was integrated using ambipolar CNT transistors. The ambipolarity of Schottky-barrier CNT FETs is a well-known phenomenon that occurs in a vacuum environment or with a top-gate oxide and electrode. A new approach that considers beneficial ambipolarity in a CNT-based CMOS circuit was proposed in which CMOS-like logic circuits (e.g., inverters and NOR/NAND gates) lacking an unreliable doping process were integrated using ambipolar CNT transistors (figure 4) that automatically configured themselves to act as n- or p-type logic gates, depending on the exchange of supply voltage (V_{DD}) and ground [22].

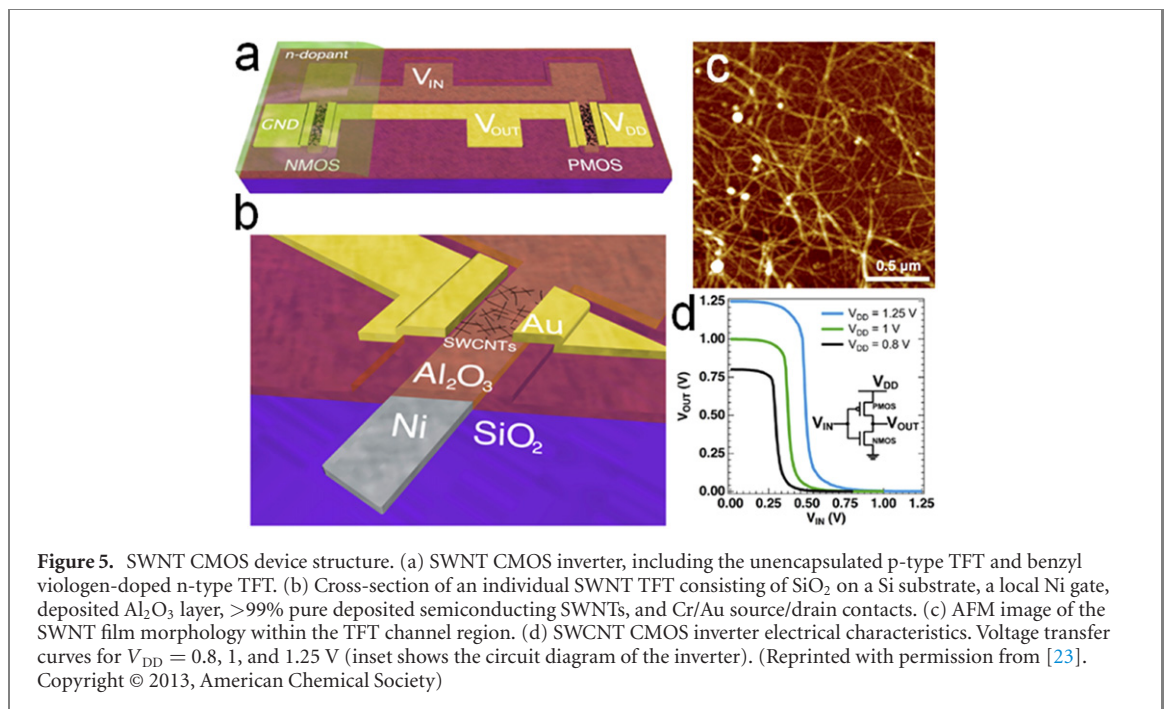
Figure 5 also shows SWNT-based CMOS logic circuits with sub-nanowatt static power consumption through the threshold voltage tuning of constituent p- and n-type SWNT transistors [23]. This behavior is enabled by a local metal gate structure that achieves enhancement-mode p- and n-type SWNT TFTs with widely separated and symmetric threshold voltages. These complementary SWNT TFTs are reported to demonstrate a CMOS inverter and NAND and NOR logic gates at supply voltages as low as 0.8 V with an ideal rail-to-rail operation, sub-nanowatt static power consumption, high gain, and excellent noise immunity. This is accomplished by precisely tuning the p- and n-type TFT threshold voltages to match the ideal conditions for an integrated CMOS device. The resulting logic gates exhibit symmetric rail-to-rail operation and excellent noise immunity, allowing the use of cascaded multiple logic gates in highly integrated circuits.



Reports suggest that the adsorption of molecules on CNTs can control their electrical properties. Similarly, CNT electrical properties can be controlled by exposing them to chemical analytes (e.g., ethanol, benzene, acetone, and toluene) for functionalization. As shown in figure 6, reversible nonlinear I - V characteristics with higher-than-usual resistance and suppressed zero-bias conductance depend on the chemical analyte. For example, when the chemical analytes interact with the CNT surface, conductivity decreases. These results confirm the chemical selectivity of CNTs and their electrical interactions with different chemical analytes [24].

Another way to generate nonlinearity may be to selectively dope the channels of SWNT networks with triethyl oxonium hexachloroantimonate and polyethylenimine to form p-i-n junctions with strong built-in electric fields. Using this method, high-performance diodes with a high rectification ratio, large forward current, and low reverse saturation current have been realized [25], and the I - V characteristics show clear nonlinear rectifying properties. An asymmetric contact was found to effectively improve p-i-n diode performance [26]. A three-dimensional electrolyte-accessible electrode structure was developed to achieve a high-performance rate in an organic electrolyte. Additionally, $\text{Ti}_3\text{C}_2\text{T}_x$ -based specially synthesized knotted CNTs, as shown in figure 7, were used to support a Ti_3C_2 network. The electrode structure was modified to simultaneously maximize ion accessibility and minimize the tortuosity of the ion transport pathways. MXene-knotted CNT composite electrodes have been reported to exhibit high capacitance with a scan rate of more than three orders of magnitude [27].

Another interesting report suggested the direct production of a CNT composite via the fermentation of yeast extract in the presence of CNT aqueous dispersion. Electrical and optical analyses demonstrated that the fermentation of beer yeast in the presence of CNTs enhanced nonlinearity, electrical conductivity, and photoconductive activity of the composite film [28].



In summary, the nonlinearity of CNT RNWs and their performance characteristics provide all the necessary properties for *in-materio* computing. In the following sections, we explain how this can be used for neuromorphic computing.

3. Neuromorphic devices and hardware on a random network of CNTs

Independent of AI, neuromorphic hardware has emerged as its own research field that focuses on neuroscience, wherein the construction of spiking neurons and their dense, complex networks is the first step of *in-materio* and in-memory computing. However, the integration density of current neuromorphic devices is much lower than that of the human brain.

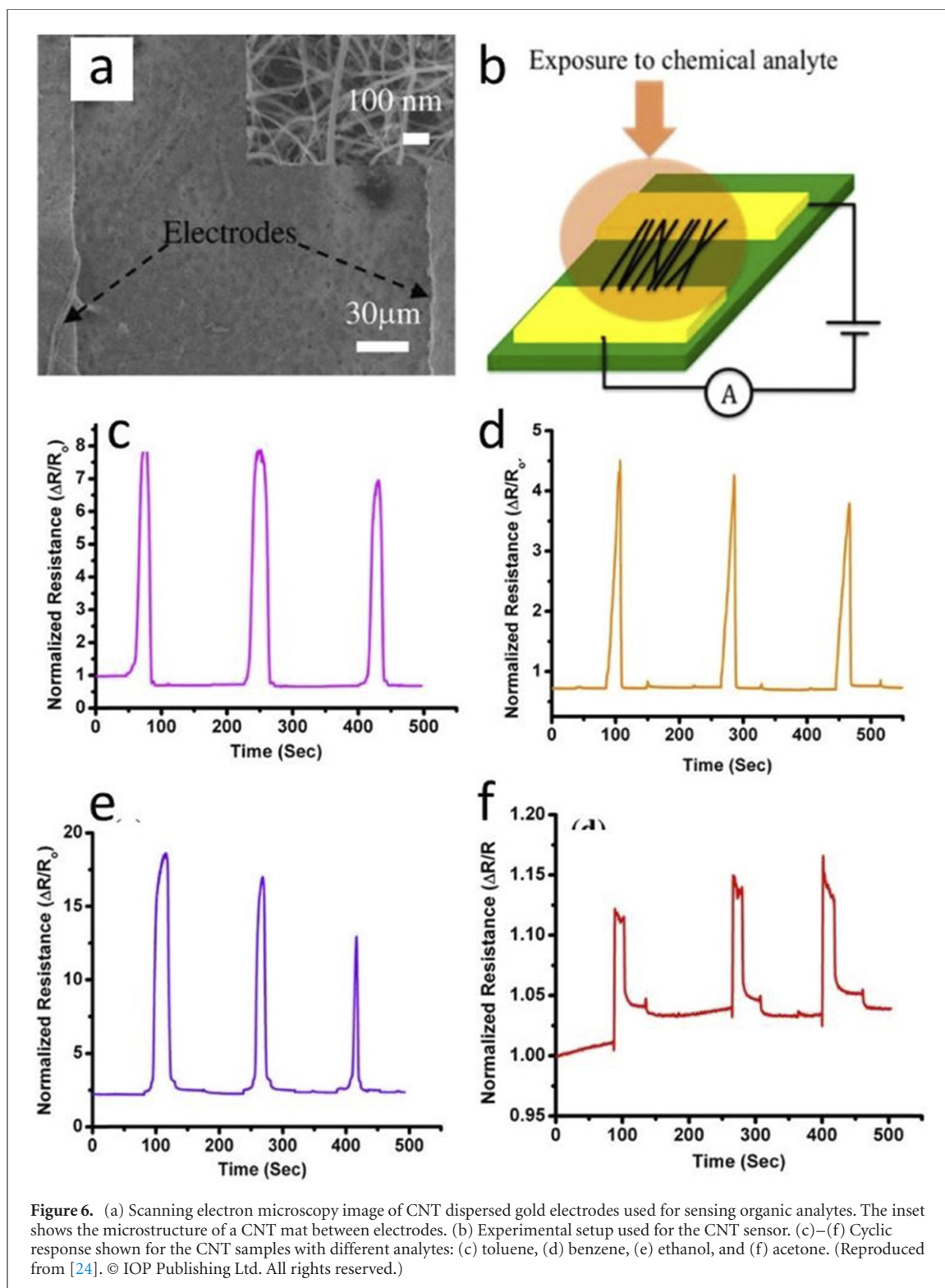
A molecular neuromorphic device comprising a dynamic and extremely dense RNW of SWNTs complexed with POM [29] was experimentally shown to generate spontaneous spikes and noise. The authors proposed an electron-cascading model consisting of heterogeneous molecular junctions that yielded results in good agreement with theory, indicating the possibility that complex functional networks could be constructed using molecular devices (figure 8).

Another approach to fabricating synaptic tendencies involves optically gated (OG) CNT FET-based synapses (figure 9) [30]. The device is controlled by light irradiation, and conductance is programmed by applying electrical pulses. A neuromorphic computing architecture was proposed using the principal advantage of the gate protection effect based on a crossbar geometry in which the gate electrodes are shared in the same row. The crossbar architecture is believed to learn several functions in a massively parallel manner while promising high reliability, high density, and fast learning.

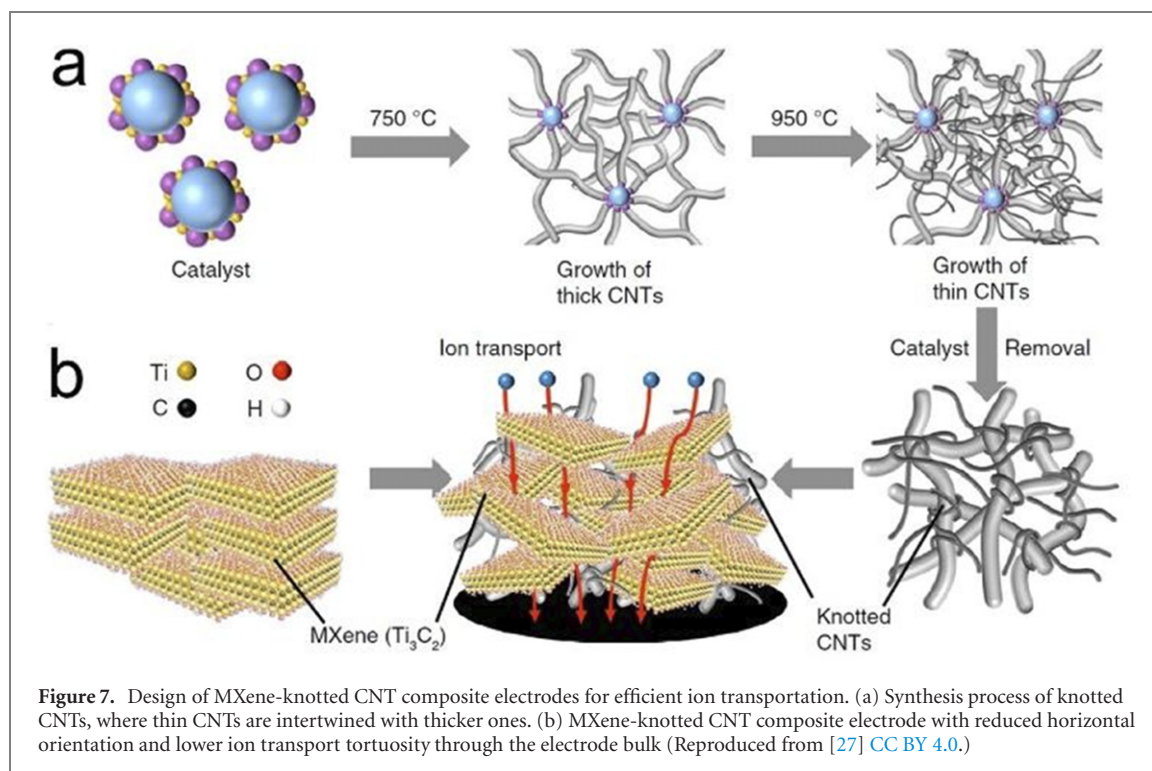
CNT synaptic transistors have also been fabricated from a hydrogen-doped PEG electrolyte sandwiched between the CNT channel and a Ti/Al top-gate electrode (figure 10) [31]. The CNT synapse was operated based on the dynamic interactions between the CNTs and hydrogen ions in an electrochemical cell (key to synaptic mechanisms). Under spike stimulation, the device emulates the dynamic logic, learning, and memory functions of a biological synapse with low energy consumption.

Although the CNT synapse has an FET structure, an oxide dielectric layer was later implanted with indium ions as the gate instead of integrating the hydrogen-doped PEG electrolyte [32]. To imitate the dynamic functions of a neuron and an axon, a CNT-based FET and a Si-based integrate-and-fire (I & F) circuit were used. By applying input spikes and using the I & F circuit to trigger output spikes, dynamic analogue post-synaptic currents and an excitatory post-synaptic current (EPSC) and inhibitory post-synaptic current (IPSC) were successfully emulated (figure 11).

In another report, an FET structure was developed to improve the capability of CNT synapses. Half of the CNT channel was converted using aluminium oxide (Al₂O₃) film, changing the CNTs from p- to n-types. As a result, a p–n junction was formed in the CNT channel, and the Schottky barrier increased between the n-type CNTs and their metal contacts. Thus, the baseline current through the CNT channel in an idle state was



significantly reduced, thus improving power efficiency. Excitatory and inhibitory synapses were emulated using multiple CNT synapses integrated with a Si-based soma circuit [33]. Additionally, a light-stimulated neuromorphic device made of printed photogate SWNT TFT-based synapses was reported. In such devices, the synaptic mechanism is induced by photogenerated carriers and trapping states in the interfaces. Under pulsed light stimulation, synaptic functions (e.g., learning, memory, and signal filtering) are successfully emulated. Multimodal optoelectronic SWNTs mixed with lead-free perovskite ($\text{CsBi}_3\text{I}_{10}$) TFTs have also been proposed. In this case, both electrical and optical pulse signals can be used together to modulate the drain currents; key synaptic functions were demonstrated. Notably, multiple artificial synapses, flash memory, and logic operations can be integrated into a single transistor. The SWNT/ $\text{CsBi}_3\text{I}_{10}$ TFT successfully implemented cognitive behaviors using Pavlov's conditioning experiment and applied the recognition of handwritten digits [34].



A novel photoneuromorphic device based on printed photogating SWNT-TFTs using lightly n-doped Si as the gate electrode was reported as similar system to the learning and memory functions of brain-inspired neuromorphic systems [35].

Poly(vinyl alcohol) (PVA) was used as the dielectric layer in a biocompatible synaptic transistor [36]. A flexible (F) transparent CNT synaptic transistor (ST)—based synapse was proposed. The behaviors of biological synapses, including spike-dependent plasticity, paired-pulse facilitation, and short- and long-term plasticity, were emulated. The F-CNT-STs exhibited high flexibility and their synaptic functions remained functional after 1000 bending cycles (figure 12).

In another fabrication approach, flexible printed SWNT TFTs using solid-state electrolyte dielectrics composed of a mixture of ion liquids and cross-linked poly(4-vinylphenol) were used as dielectric layers [37]. These devices can simulate basic synaptic plasticity such as EPSC and paired-pulse facilitation, as well as their inhibitory characteristics. It exhibits good stability and mechanical flexibility, and the change in the EPSC curve is almost negligible before, during, and after bending (figure 13).

A CNT transistor was used to demonstrate an artificial tactile sensor system [38], exhibiting a semi-volatile characteristic that can switch the operation mode (volatile or nonvolatile) according to the bias condition. As a semi-volatile device, both sensory neurons and the perceptual synaptic network were implemented as a single device. The tactile sensor system distinguishes temporally correlated pressure stimuli and extracts features of the tactile patterns for pattern recognition (figure 14).

A unique study on neuromorphic devices was later conducted through which more attention was paid toward utilizing biocompatible and biodegradable materials [39]. A degradable chlorophyll-a/SWNT synaptic transistor was developed on a PVA substrate to provide a naturally biodegradable and water-soluble device to demonstrate zero e-waste (figure 15). Key synaptic functions, including EPSC, paired-pulse facilitation, transition from short- to long-term memory, and learning and forgetting experiences, were successfully realized with this device. The device dissolved with rainfall and completely decomposed after 5 min.

4. *In-materio* physical reservoir computing (RC) devices on CNT random network

Hereafter, we describe reservoir computing (RC) devices based on material engineering. Several approaches have been developed to complement current AI hardware with material devices. An artificial neural network (ANN) inspired by the biological neuromorphic behavior of the brain is shown in figure 16(a). Most current AI systems comprise feedforward-propagating neural networks (NNs). Each node computes a nonlinear transformation of the sum of the products between the incoming signals and their synaptic weights, plus an additional bias term (red circles in figure 16(a)). When this kind of system contains more than three hidden (middle) layers, it qualifies as deep learning [40]. Unlike feed-forward propagation NNs, recurrent NNs (RNNs) can

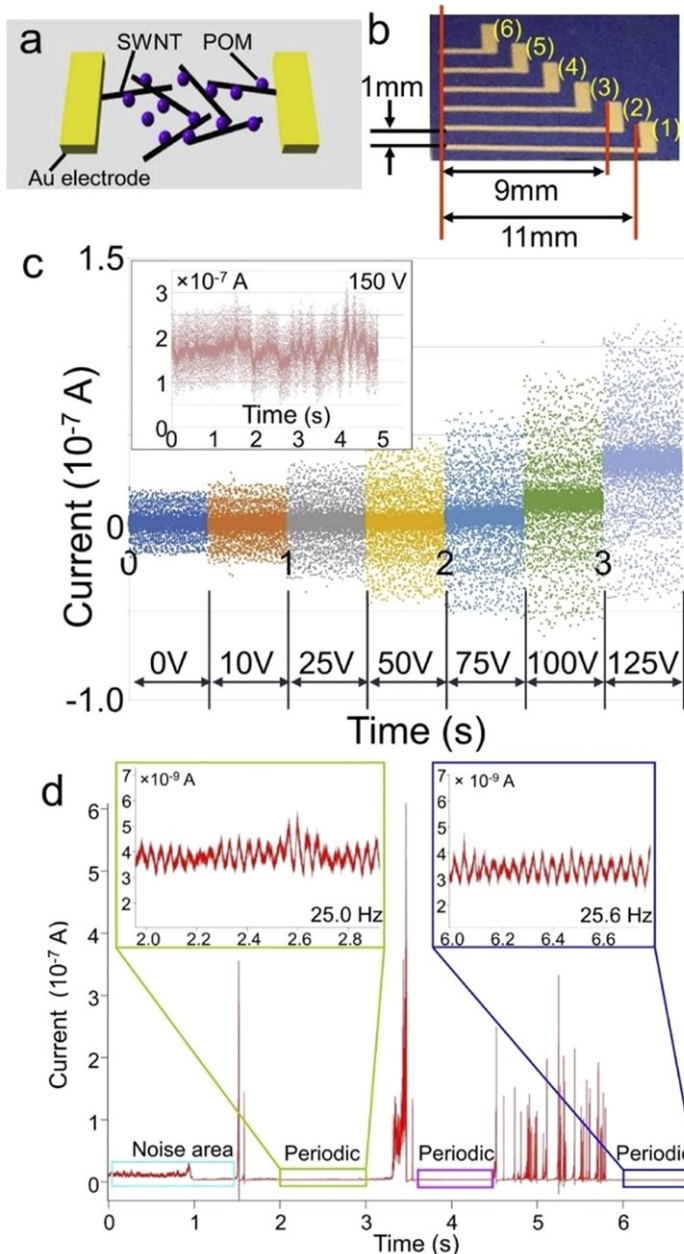
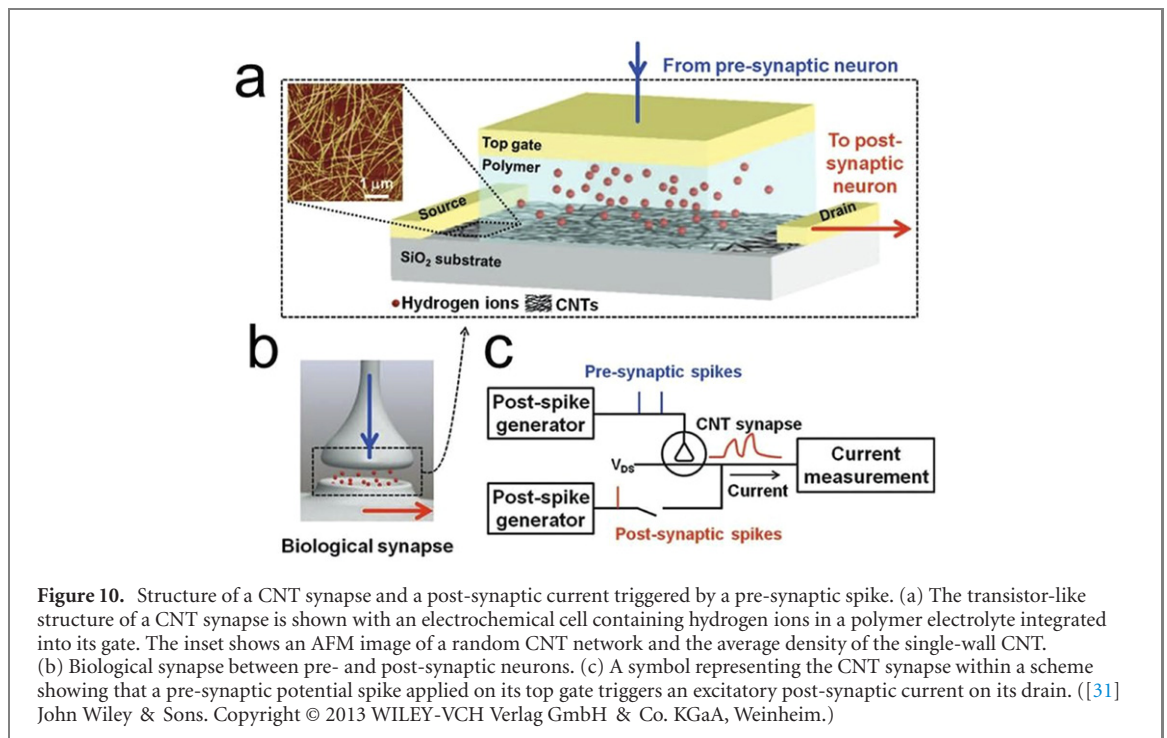
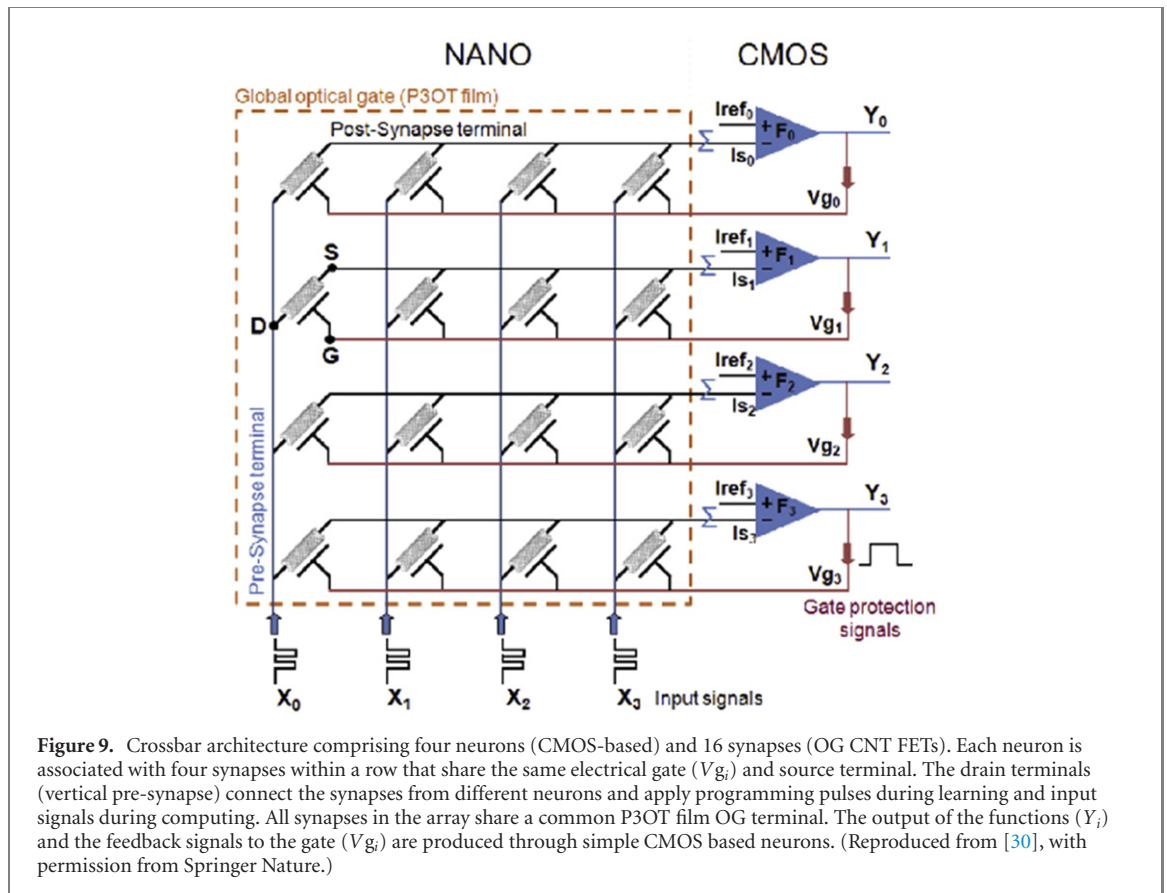


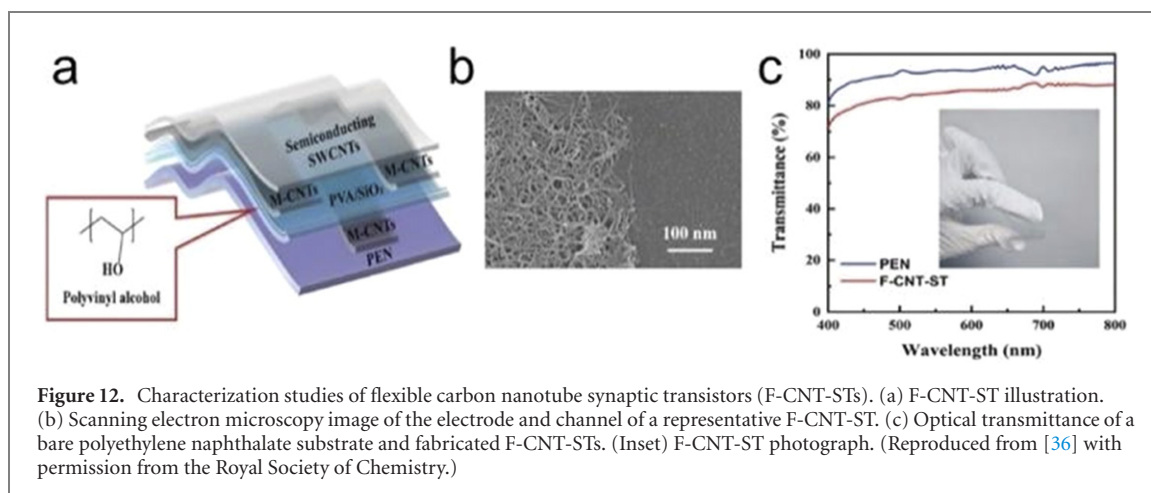
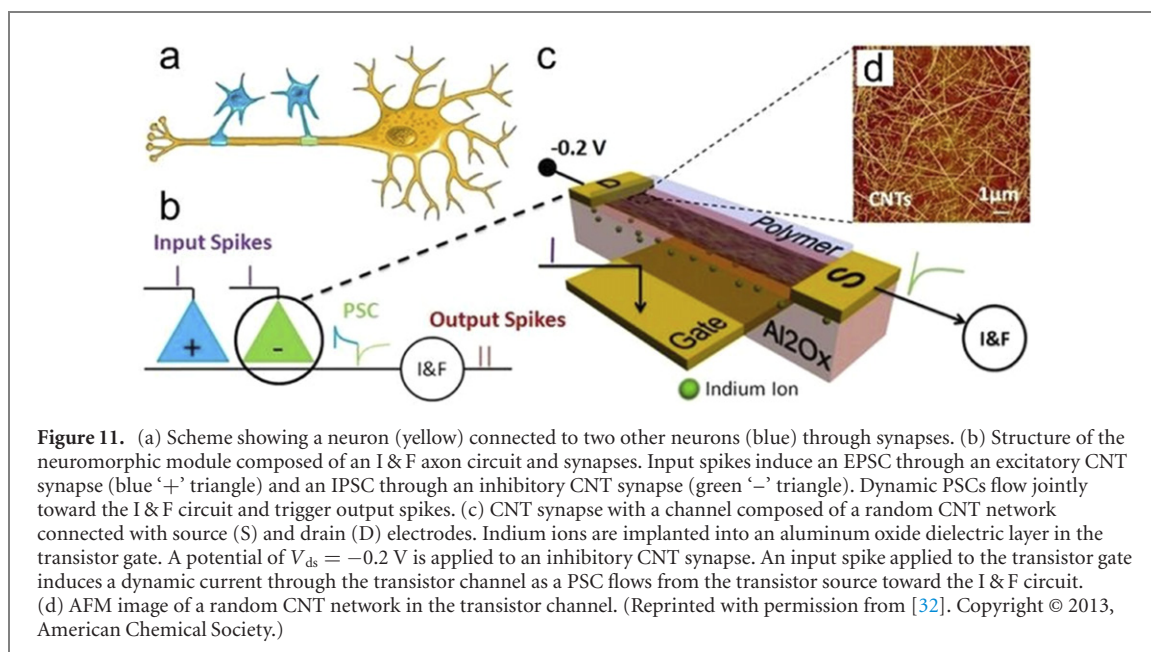
Figure 8. Experimental setup and noise generation of a SWNT phosphomolybdic acid (POM) network. (a) SWNT/POM complex network. Yellow cuboids, black tubes, and purple spheres represent terminal electrodes, SWNTs, and POM particles, respectively. (b) Substrate covered with the SWNT/POM complex that includes six electrodes. (c) Sampled current density over time, representing current magnitude distributions with the bias voltage increasing stepwise across electrodes from 0 to 125 V for the network. (Inset) Current becomes unstable at 150 V. (d) Time dependence of the current under humidity. (Inset) Magnification of periodic base current modulation. (Reproduced from [29] CC BY 4.0.)

use their internal state (memory) to process any sequence of inputs, meaning that some information from a given node can be fed back into the original, as shown by the blue circle arrows in figure 16(a). This allows them to exhibit temporal dynamics [41] suitable for tasks such as non-segmented, connected handwriting [42] and speech recognition [43, 44]. RC is a special RNN case, as shown in figure 16(b); it was developed from echo-state networks (ESNs) [45, 46] and liquid-state machines [47] as its information-processing framework [48, 49]. The ESN provides an architecture and a supervised learning principle for RNNs for the RC system, in which the hidden layer is treated as a black box, indicating that the internal weight of the network is fixed. Strong nonlinearity, high dimensionality, and higher memory are necessary properties of an RC system. Learning is conducted only in the output layer through simple linear regression. The *in-materio* and physical RC is reported to be in good agreement with RC theory. Hence, there have been many interesting reports about the materials needed to develop RC devices.

The high-dimensional nonlinear transformation of the input signals obtained as a function of the output signals can be treated equivalently to the information generated when a software-designed NN architecture



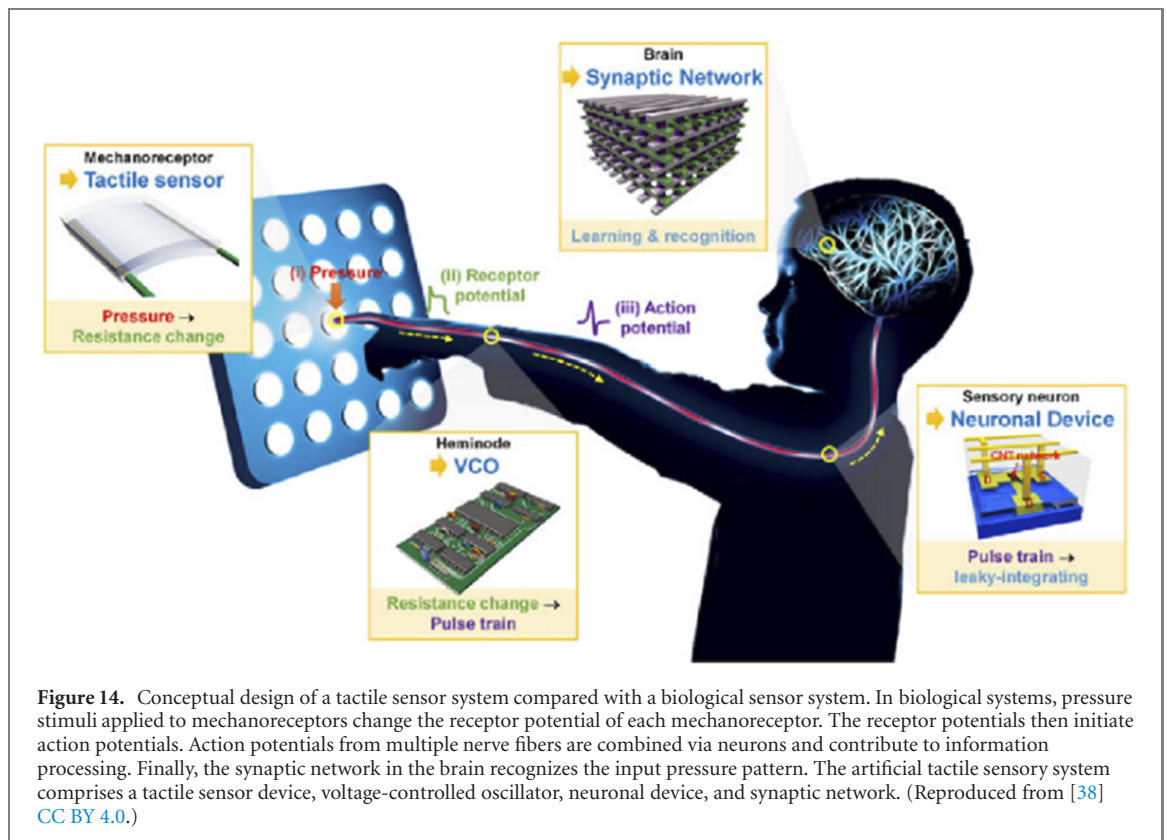
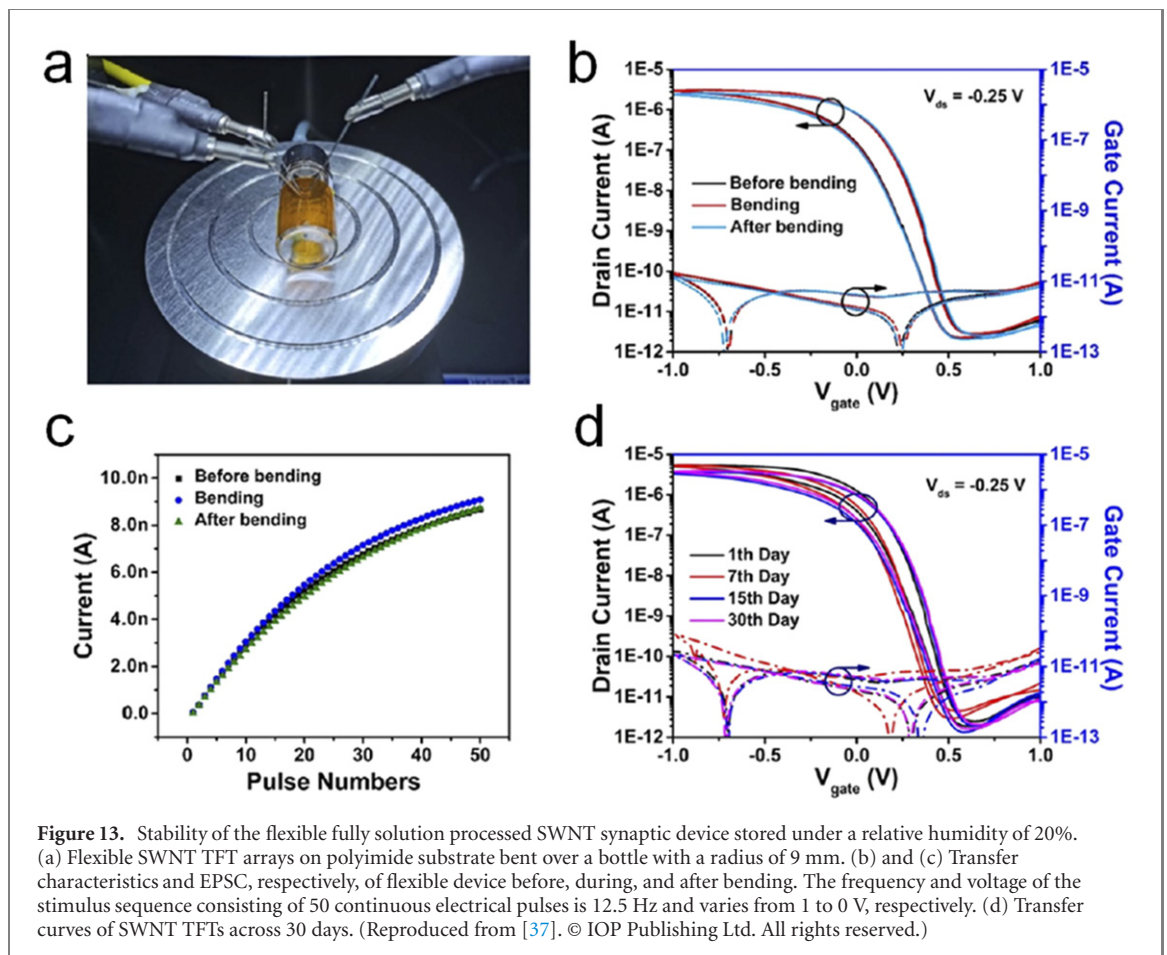
operates with a nonlinear activation function. Therefore, hardware can be implemented by simply learning these output signals without the need for a separate information processor. Although many such hardware NN models [50] have been studied, RC is novel and has only recently attracted significant attention (figure 16(b)) [51–54] owing to its straightforward framework for processing time-series data. The execution of RC learning for time-series prediction tasks has been applied to atomic switch networks (ASNs) [55–57], memristor networks [58], CNT/polymer composites [59, 60], NP aggregation [57], polymer network systems [61],



optoelectronic systems [62, 63], soft bodies [64, 65], spintronics [4, 66], and water-tank systems [67]. The efficacy of each RC material is derived from the intrinsic reservoir property [53, 54] of recurrent nonlinear high-dimensional dynamics analogous to the human brain [10]. Irrespective of their material and fabrication diversity, their inherent dynamical complexity enables an easy input-driven computation of RC tasks with only readout trainability. Among the many physical systems, RCs with ASNs and CNTs have a promising future as large-scale bioinspired computers owing to their brain-like physicality and solution-processable RNW integration. Therefore, materials with such dynamics and physical architectures are being explored, including random SWNT networks with porphyrin POM [29].

As shown in figure 8, SWNTs are a source of noise and when functionalized with redox-active POM, they can undergo changes in their conductive states, generating brain-like random fluctuations and neuronal spike-like signals [29]. Utilizing intrinsic dynamics, an RNW structure was simulated and rudimentary learning ability through external feedback was illustrated with a theoretical RC model (figure 17(a)). Complex nonlinear dynamics were chosen from randomly selected POM molecules within the network, specifically from the source/drain side and FORCE (algorithm) learning was applied to optimize output weights to carry out the RC benchmark task of nonlinear autoregressive moving average (NARMA)-10 time-series prediction (figures 17(b)–(d)). Task learning was inferred by evaluating the normalized root mean-square deviation (NRMSD), where the lowest NRMSD implies the best optimization [30].

As an extension work of reference [29], reservoir performance of SWNT/POM was experimentally evaluated [68]. SWNT/POM with a polybutylmethacrylate (PBMA) composite was used to experimentally verify the RC task using NARMA-10. Thin composite films were prepared by ultrasonically mixing SWNTs, POM, and PBMA and drop-casting them onto a 10×10 grid microelectrode array. A laboratory-built experimental computing platform was designed to benchmark the supervised NARMA-10 time-series prediction. By



utilizing the nonlinear current dynamics of SWNT/POM, NARMA-10 was successfully implemented with a normalized root mean-square error of 0.08, compared with the 0.19 score of the SWNT reservoir alone [69].

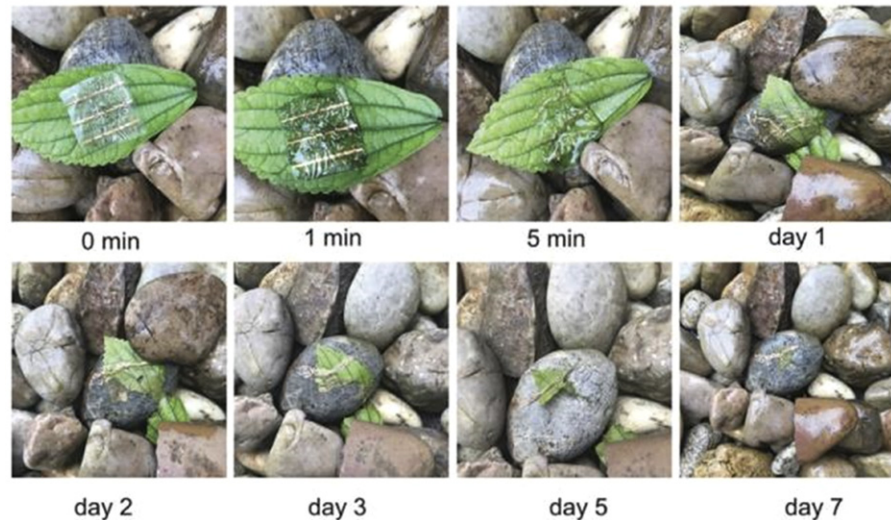


Figure 15. Demonstration of the degradable process of chlorophyll-a SWNT composite transistor array. ([39] John Wiley & Sons. © 2021 Wiley-VCH GmbH.)

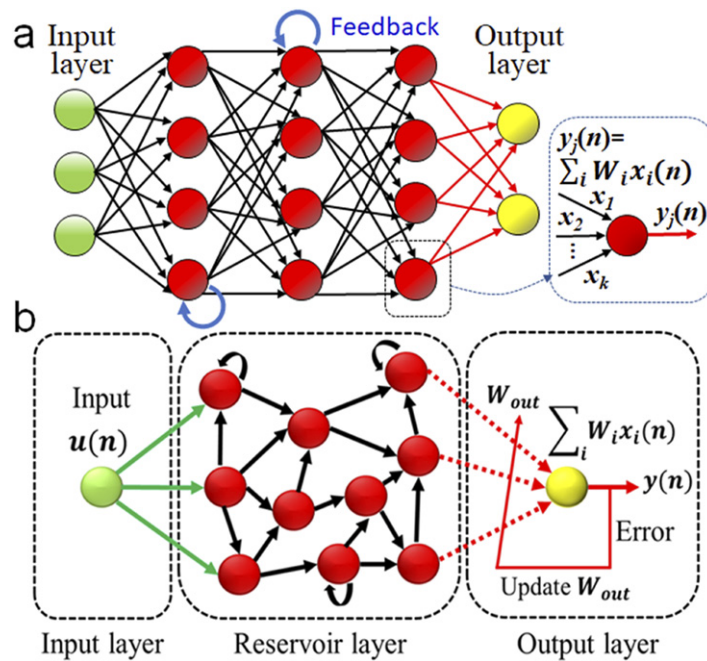
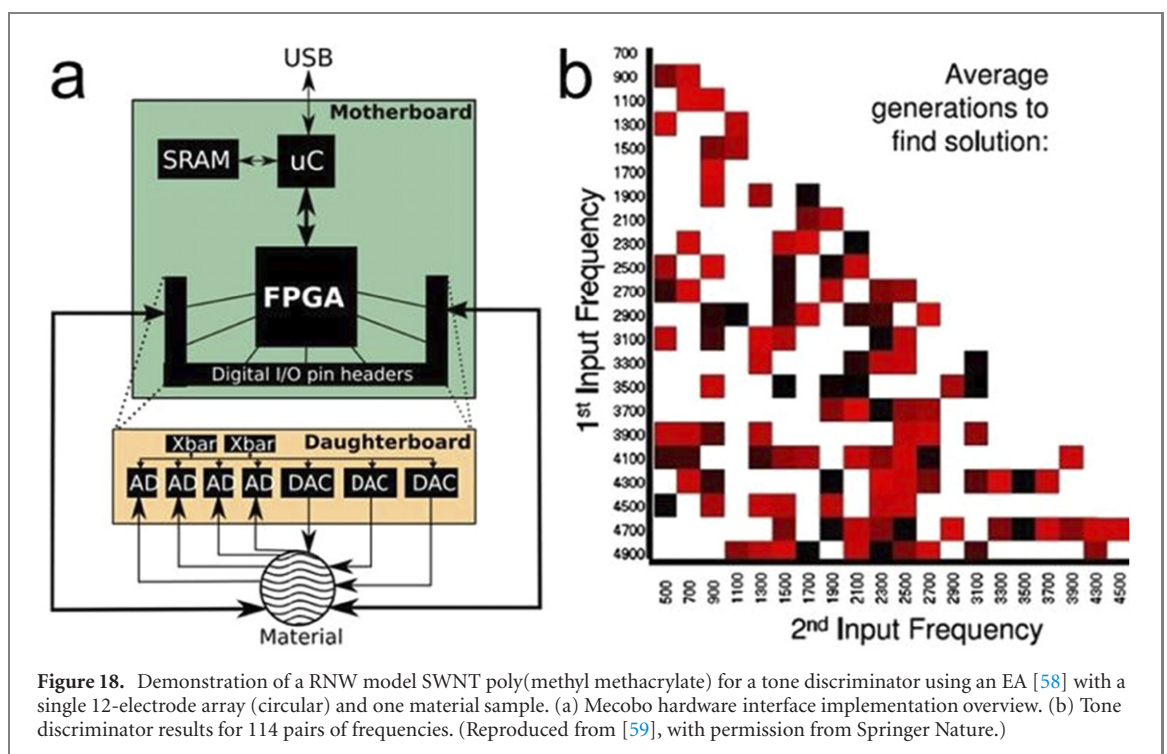
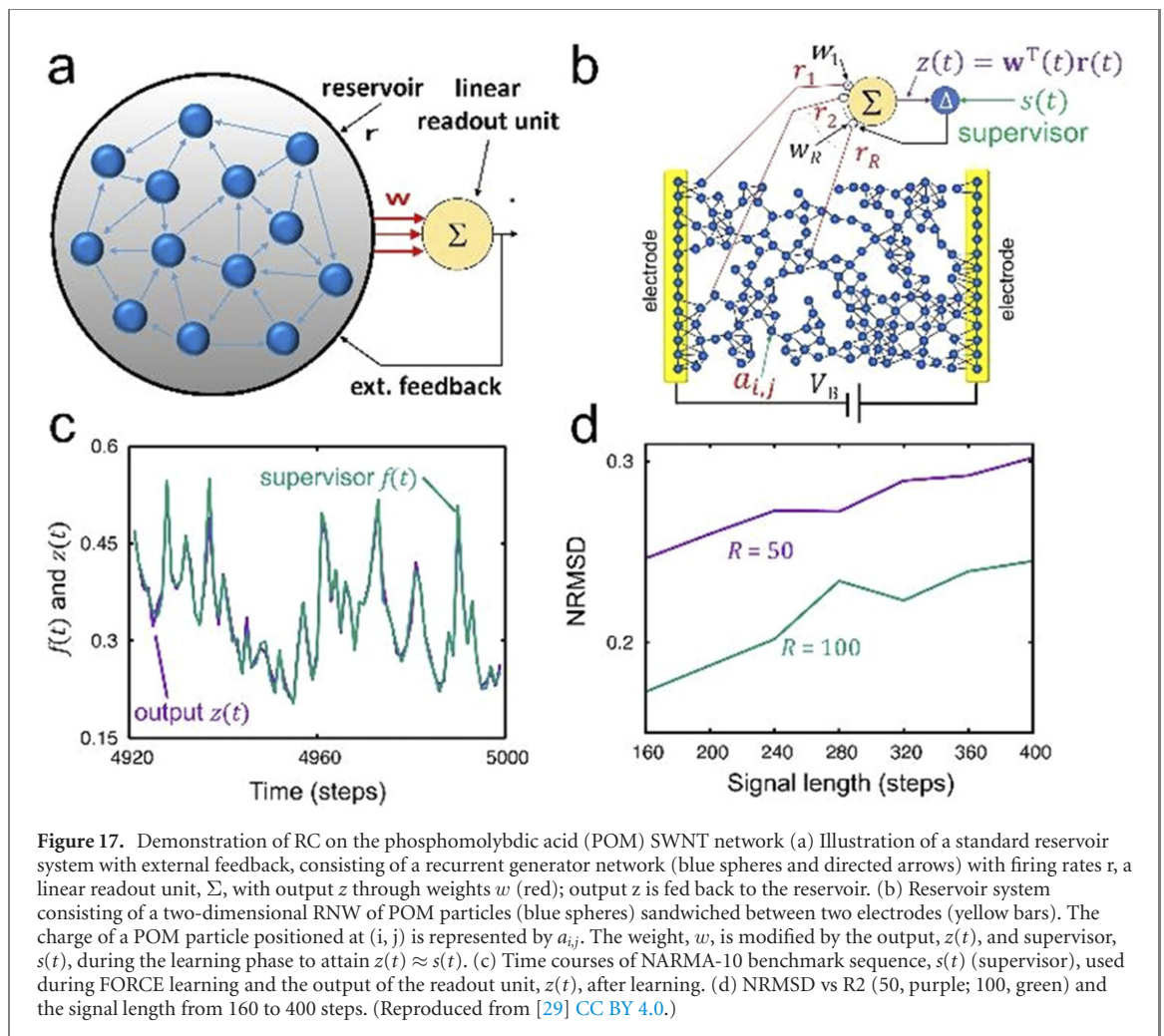
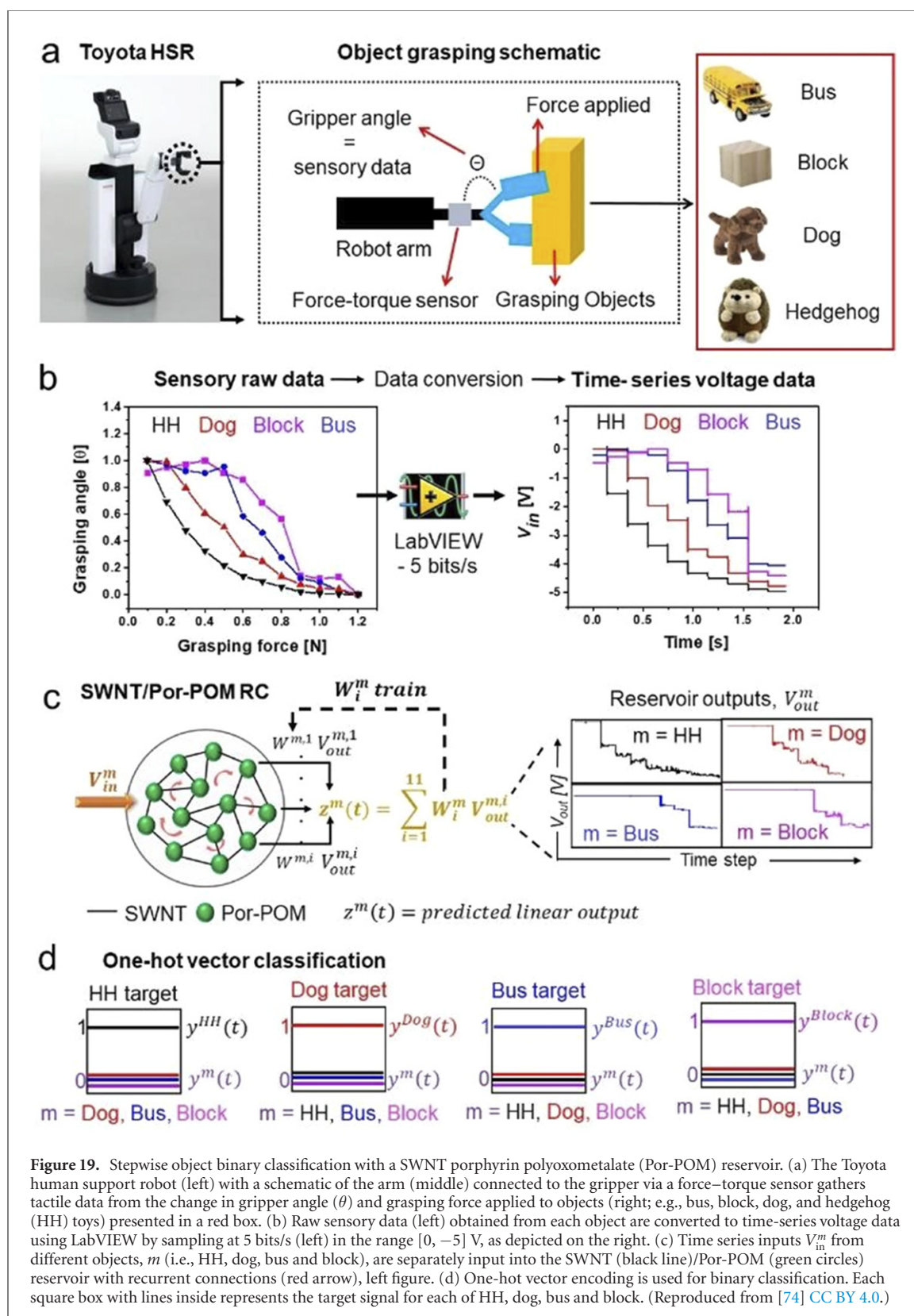


Figure 16. (a) An ANN. A recurrent take NN allows for the feedback of information (blue circle arrow) at the nodes (red circles). When signal has feedback at the nodes, the system is called as RNN. (Inset) The sum of products for all incoming signals are calculated at all nodes. (b) Reservoir network which is a kind of RNN. All nodes having non-linearity are connected randomly. Calculations in the middle layer are not required by treated as a black box. Learning is achieved only at the output layer.

In another report, a composite SWNT polymethyl methacrylate (PMMA) was used to construct an RC device using a micro-electrode array architecture (figure 18(a)) integrated into a Mecobo hardware platform consisting of field-programmable gate array-driven input/output controllers used to evolve the voltage outputs (figure 18(b)). Mecobo hardware was also interfaced with an evolutionary algorithm (EA), a genotype-based biological model that optimizes the output electrode response for a tone discriminator RC benchmark task. Generally, in a tone discriminator, two inputs of different frequencies are classified by two output classes labeled '1' for low-frequency input and '2' for high-frequency input. The RC operation was performed in real-time, and apart from the inputs and outputs, specific voltages were applied to the rest of the electrode pads used to configure the device behavior. The configuration voltages affect the electrical behavior of the CNT-polymer material, and the interaction induces certain voltages on the output electrode. The output was optimized with EA through a fitness score, where the highest score implies valid output class optimization for discriminating the input frequency tone [59].





To demonstrate performance, the same device was used to apply the RC tasks of NARMA-10, waveform generation, and memory capacity. The results highlight the versatility of the device for RC benchmark performance by controlling and optimizing the voltage outputs with varying degrees of SWNT/PBMA concentration [60]. OR and AND Boolean logic gates and a half-adder operation were also accommodated by varying SWNT concentrations. The upper limit of the linear increase in viscosity and conductivity against the concentration of SWNTs of approximately 1% showed the best operational performance [70]. A simulation attempt was made to solve the traveling salesman problem [71, 72], where Pi-swarm robots were tasked with moving along a maze to reach an end goal without colliding [73].

In another report, it was shown that a physical RC platform consisting of a recurrent SWNT-porphyrin polyoxometalate complex network successfully executed fundamental reservoir properties of nonlinearity, higher harmonic generation, and $1/f\gamma$ power-law information processing [9, 74, 75], where $1/f\gamma$ implies a scale-free network distribution with self-organized criticality analogues to the human brain. A one-hot vector target-based supervised object classification task using tactile input [74], performed by a Toyota human support robot [76], was executed by following a known Robo Cup worldwide [77] task. This was the first report of an RC device consisting of a CNT RNW reservoir device directly induced in a robot for a recognition task (figure 19).

A room-temperature demonstration of an *in-materio* RC with the same material was performed [78] in which Boolean OR, AND, NOR, NAND, XOR, and XNOR functions were reconstructed with an >90% accuracy via the supervised training of linear voltage readouts. The RC prerequisite of an echo-state property and a recurrent connection enabled consistent performance over multiple test datasets and time-shifted target sequences.

We expect that an *in-materio* AI system fabricated using material hardware will be realized in the next generation of computing devices.

5. Conclusion

In this article, we surveyed the historic results of initial CNT electrical measurement, the electrical nonlinearity of individual CNTs, and those complexed with molecules, neuromorphic devices, and hardware used for RNWs of CNTs and RC devices. We recounted the processes by which CNT RNWs obtain intelligence so that they can be used for *in-materio* computing. The surveyed studies demonstrate the potential of CNTs and their complexes as candidates for future AI computing and robotics. Of course, much work is still needed before such devices can become commercialized, but the path is clearing daily. Moreover, *in-materio* computing is not necessarily bound to CNTs; many other media are being investigated. We leave the review of other *in-materio* compounds for RC capabilities to others. In the meantime, this review clearly demonstrates how material engineering can play a role in the development of low-energy AI systems.

Acknowledgments

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Data availability statement

No new data were created or analysed in this study.

ORCID iDs

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