Nano Energy 48 (2018) 575–581

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Full paper

Ultrasensitive artificial synapse based on conjugated polyelectrolyte

Wentao Xu[a,d], Thanh Luan Nguyen[b], Young-Tae Kim[c], Christoph Wolf[c], Raphael Pfattner[d], Jeffrey Lopez[d], Byeong-Gyu Chae[c], Sung-Il Kim[a], Moo Yeol Lee[e], Eul-Yong Shin[f], Yong-Young Noh[f], Joon Hak Oh[e], Hyunsang Hwang[c], Chan-Gyung Park[c], Han Young Woo[b], Tae-Woo Lee[a,*]

[a] Dept. of Materials Science and Engineering, Seoul National University, 1 Gwanak-Ro, Gwanak-gu, Seoul 08826, Republic of Korea
[b] Department of Chemistry, Korea University, Seoul 02841, Republic of Korea
[c] Dept. of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Gyungbuk 37673, Republic of Korea
[d] Department of Chemical Engineering, Department, Stanford University, Stanford, CA 94305, United States
[e] Dept. of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Gyungbuk 37673, Republic of Korea
[f] Department of Energy Materials Engineering, Dongguk University, 30, Pildong-ro 1-gil, Jung-gu, Seoul 04620, Republic of Korea

ARTICLE INFO

Keywords:
Neuromorphic devices
Memory
Dipole reorientation
Ion migration
Sensitivity

ABSTRACT

Emulating essential synaptic working principles using a single electronic device has been an important research field in recent years. However, achieving sensitivity and energy consumption comparable to biological synapses in these electronic devices is still a difficult challenge. Here, we report the fabrication of conjugated polyelectrolyte (CPE)-based artificial synapse, which emulates important synaptic functions such as paired-pulse facilitation (PPF), spike-timing dependent plasticity (STDP) and spiking rate dependent plasticity (SRDP). The device exhibits superior sensitivity to external stimuli andlow-energy consumption. Ultrahigh sensitivity and low-energy consumption are key requirements for building up brain-inspired artificial systems and efficient electronic-biological interface. The excellent synaptic performance originated from (i) a hybrid working mechanism that ensured the realization of both short-term and long-term plasticity in the same device, and (ii) the mobile-ion rich CPE thin film that mediate migration of abundant ions analogous to a synaptic cleft. Development of this type of artificial synapse is both scientifically and technologically important for construction of ultrasensitive highly-energy efficient and soft neuromorphic electronics.

1. Introduction

An artificial intelligent system that fully realizes the performance of a human brain would consist of a huge number of artificial synapses [1,2]; for such a system to be practical, the extreme sensitivity and high-density integration of the synapses need to be emulated [3–5]. Additionally, flexibility and biocompatibility of polymeric materials would facilitate the construction of electronic-biological interfaces, bio-implanted electronics and soft robotics. In response to these requirements, synaptic functions have been fabricated using soft materials such as Nafion [6], chitosan [7] and PEDOT:PSS [8]. Recently, ion-gel-gated polymer semiconductor nanowire transistors and conducting polymer/organic-inorganic perovskite double layer two-terminal devices also demonstrated synaptic functions using electric-field-induced ion-migration and trapping [5]. However, development of materials that can realize synaptic functions in a single soft working component, and that possesses high sensitivity is still required.

Conjugated polyelectrolytes (CPEs) are polymers composed of a conjugated backbone and aliphatic side chains that end with ionic functionalities [9]. The special chemical structure allows stable photophysical properties and biocompatibility, and therefore broad applications to biosensing, bioimaging and delivery of therapeutics [10]. Ionic pairs of an ammonium ion and a halogen ion serve as dipoles, which reorient to align with an external electric field [11]. Relatively strong electric field can cause dissociation of the ionic pair and the migration of mobile ions [12]. These dipole reorientation and ion migration processes are essential properties to contribute to consecutive modulation of the electrical responses, and are suitable for emulating synaptic functions.

Here, we report the fabrication of an artificial synapse that used a conjugated polyelectrolyte functional layer to achieve analogous plasticity of a biological synapse. The electronic device successfully emulated synaptic working principles, such as excitatory postsynaptic current, paired-pulse facilitation, spike-timing dependent plasticity and

* Corresponding author.
E-mail addresses: twlees@snu.ac.kr, taewlees@gmail.com (T.-W. Lee).

https://doi.org/10.1016/j.nanoen.2018.02.058
Received 27 September 2017; Received in revised form 7 February 2018; Accepted 28 February 2018
Available online 27 March 2018

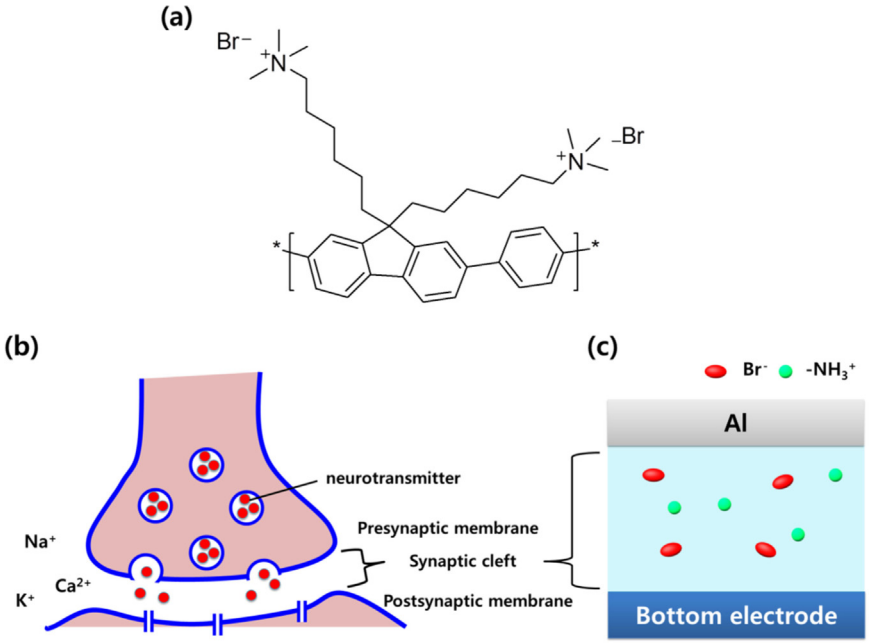


Fig. 1. Schematic demonstrations of a) Chemical structure of CPE-Br with a conjugated structure in the polymer backbone and ammonia functional group on the side chains that bond to bromides. b) A natural synapse with presynaptic membrane, postsynaptic membrane and the synaptic cleft in between. c) Geometry of a CPE-Br artificial synapse.

spike-rate dependent plasticity. It exhibited superior sensitivity to external stimuli of down to 10 millivolt, and low-energy consumption level of femtojoule per synaptic event. These properties were based on an hybrid working mechanism that dipole reorientation and ion migration underlie short-term plasticity, while resistive switchable properties of the ultrathin film enabled long-term plasticity.

2. Results and discussion

The chemical structure of bromide-containing CPE (CPE-Br) is shown (Fig. 1a). The device structure is Al/CPE/bottom/electrode. A Pt layer is deposited to protect the sample during focus-ion-beam (FIB) process for making TEM samples. Bromide is in the middle of halides in periodic table and is selected as a representative material of halides for this study. CPE-Br synapses in a simple sandwiched structure of Al/CPE-Br/n+Si were fabricated to emulate essential working principles of a synapse (Fig. 1b,c) [13]. The typical device showed a sandwiched CPE-Br layer with a thickness ~ 40 nm (Fig. 2a). The conjugated backbone facilitates charge-carrier transport. The CPE-Br thin film emulates the synaptic cleft between presynaptic and postsynaptic membranes, where motion of neurotransmitters occurs. The thickness is quite similar to that of the biological synaptic cleft (20-40 nm). The surface of CPE-Br thin film is smooth with a root-mean-square roughness of 1.01 nm (Fig. 2b), which ensures uniform characteristics of electronic devices.

A biological synapse encodes information as a modulation of synaptic weight at a range of levels. Therefore, to realize such multilevel memory, a consecutively tunable current signal is required. The current signal of the CPE-Br thin film was modulated by applying consecutive external pulses that induce reorientation of dipoles and migration of ions. Arrhenius plot (Fig. 2c) of the device features two linear regions with distinct slopes. The change in slope implies a change in activation energy from E_a = 19.2 meV at T < 250 K, to E_a = 62.5 meV at T > 260 K. This change in E_a implies the coexistence of at least two conduction mechanisms at room temperature. A primary change in the CPE-Br thin film would be dipole reorientation in response to an external electronic field. Because the ammonium ions are connected to the conjugated backbone by a flexible chain, dipoles reorient and move around the aromatic backbone. E_a of this process should be small; we assign the low E_a = 19.2 meV to it. In the CPE-Br layer, the bromide has ionic interaction with ammonium ions. Increasing the strength or number of pulses could cause decoupling of the ionic pairs, and induce bromide migration. We assign the high E_a = 62.5 meV to this process. This corresponds to the glass transition temperature (T_g) of the CPE-Br (Fig. 2d). Above T_g the motion of the aliphatic side chains is released and the two effects coexist in the at room temperature to cause the change in conductance and formation of electrical double layers (EDL) that release charges after electrical pulses (Fig. S1), underlying temporal change in conductivity and short-term plasticity. It has been discussed in previous reports that the ions migrate and dipoles align in response to electric field [14–17]. Because migration of electrons is several orders of magnitude faster than migration of ions [18], the measured current at different distributions of inner gradients represents electronic current. Non-volatile memories based on mixed ionic-electronic conduction have been reported [19], but consecutive modulation of resistivity of thin CPE-Br thin film upon external stimuli for use in neuromorphic electronics has not been studied; this property would be an important advance toward applications of mixed ionic-electronic conduction in artificial synapses.

Short-term memory can be realized by temporary modulation of synaptic strength. In the CPE-Br-based artificial synapse, external pulses are applied to metal top electrodes to emulate the arrival of presynaptic spikes at the presynaptic membrane. The pulses induce dipole reorientation and ionic migration in the CPE-Br thin film to trigger excitatory post-synaptic current (EPSC) at a continuous reading bias on the bottom electrode, i.e., n+Si. After the pulses, dipole orientations recover, and ions back diffuse so that the current quickly decays to the resting state (Fig. 3a).

In a biological synapse, successive stimuli can cause increase in the number of neurotransmitters released from presynaptic membrane into the synaptic cleft. This increase then induces an increase in the number of opened gates of receptors and consequent increase in ionic flux through the postsynaptic membrane. Analogously, successive pulses consecutively modulate EPSC by increasing the number of accumulated aligned-dipoles and the number of migrated ions in the electronic device. In the CPE-Br-based synapse, EPSC increased as the number of pulses (e.g., 2 or 3) increased (Fig. 3a). The phenomenon that a superimposed peak induced by a second pulse is higher than the peak triggered by the first pulse is known as paired-pulse facilitation (PPF). In this process, the second pulse is identical to and closely follows the first pulse. The phenomenon weakened as the interval between the two pulses was increased (Fig. 3b). Increase in the number of pulses to 10 significantly increased EPSC as compared to EPSC triggered by a single

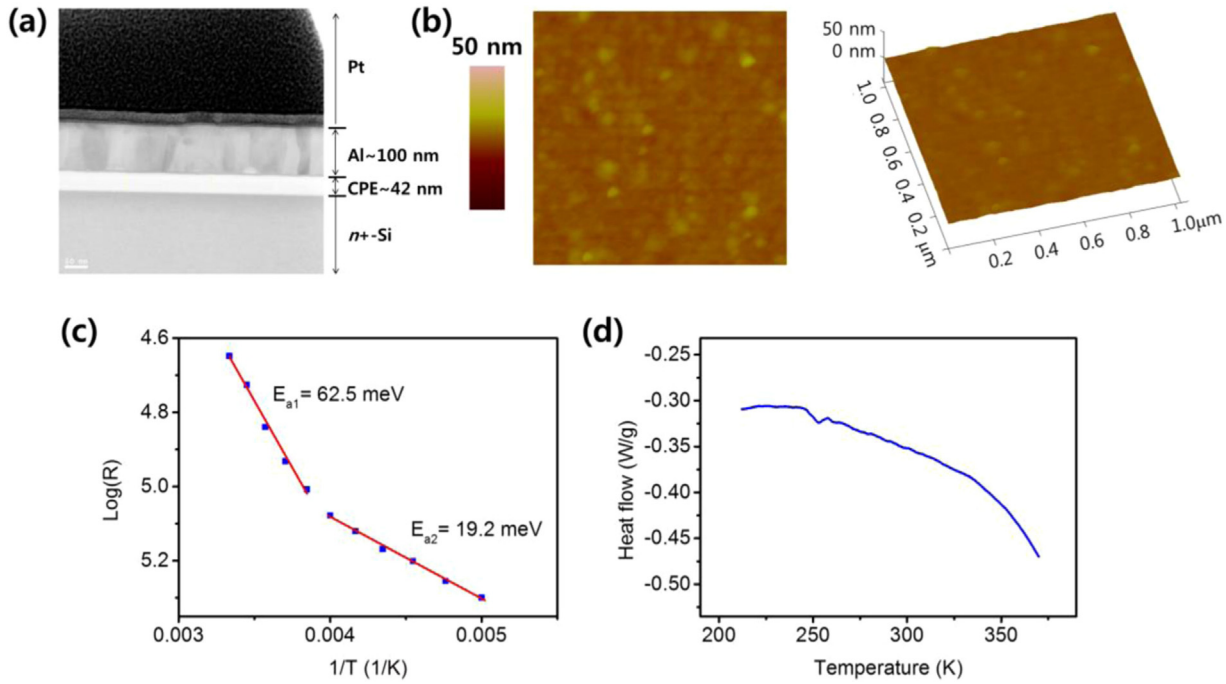


Fig. 2. a) TEM image of the cross-section of the device that was cut using Focused Ion Beam. b) AFM images of surface morphology of CPE-Br thin film. c) Logarithm of resistance as a function of the reciprocal of absolute temperature for CEP thin film. d) DSC analysis of CPE-Br polymer as obtained at 10 °C/min. Glass transition temperature between 250 and 260 K was observed.

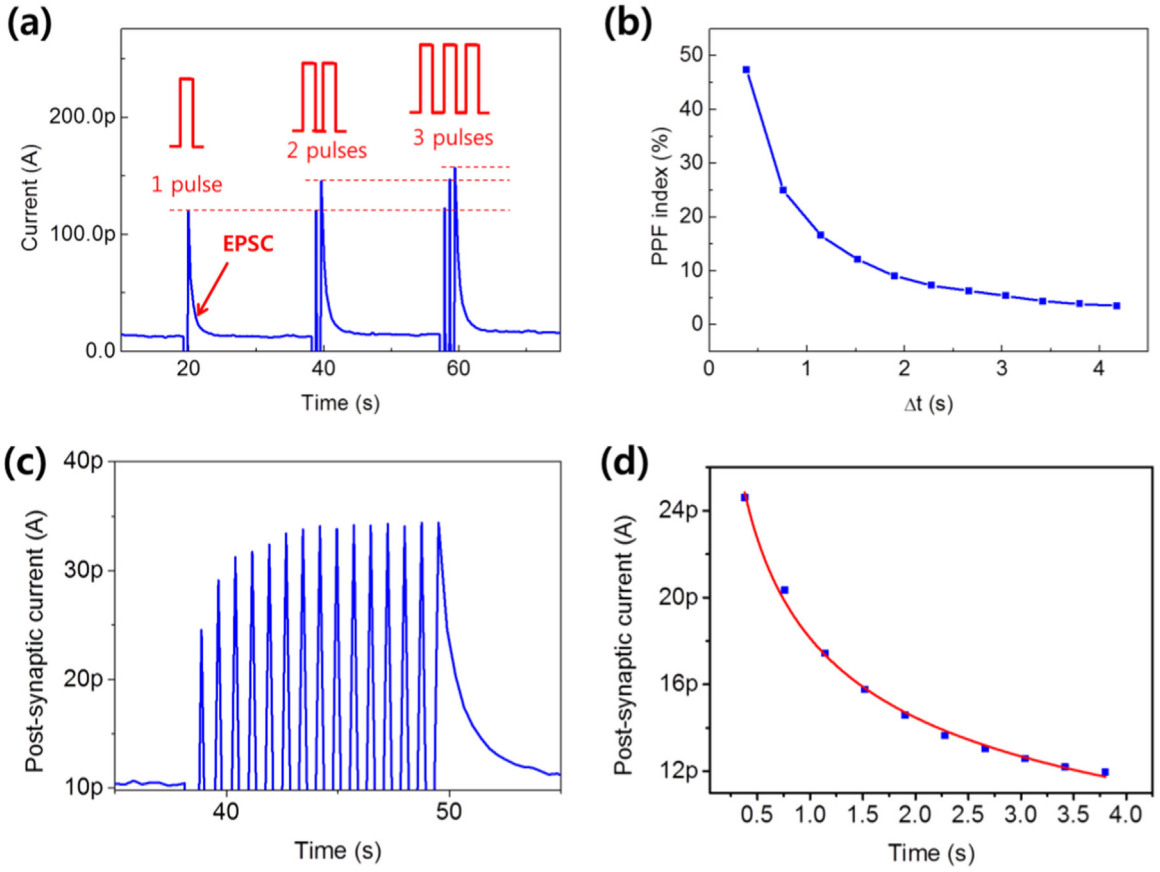


Fig. 3. a) EPSC triggered by an applied external voltage pulse, and current increase achieved by two and three successively applied pulses, emulating a biological process of paired-pulse facilitation (Reading bias 0.1 mV, pulse amplitude 0.5 mV). b) PPF index as a function of interval between two pulses. b). e) PPF index vs. interval between two pulses. c) increased EPSC as triggered by 10 successive pulses (Reading bias 0.1 mV, pulse amplitude 0.1 mV). d) Fitting of the current retention to the curve of forgetting.

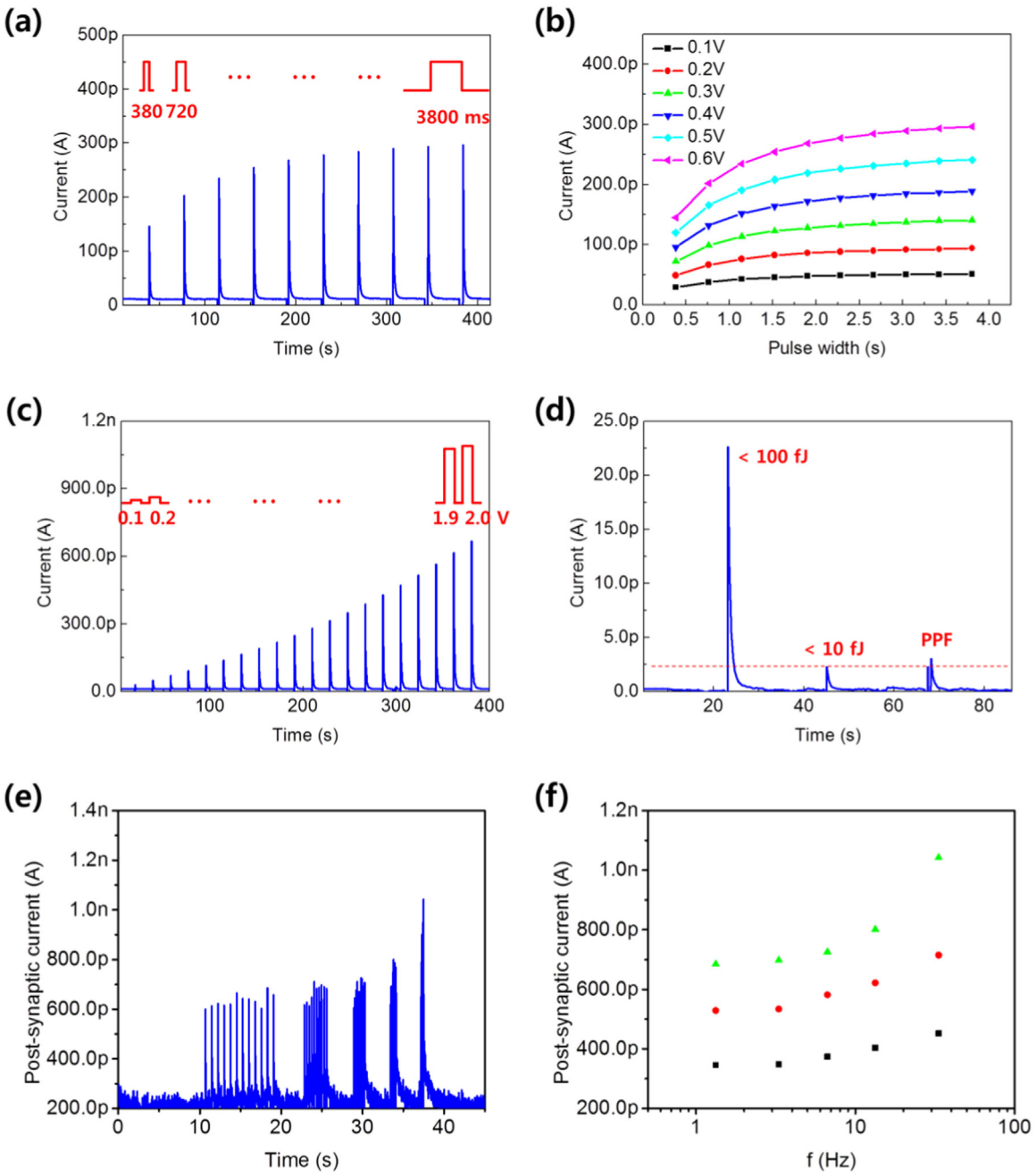


Fig. 4. a,b) Spiking-duration dependent plasticity (pulse amplitude = 0.6 V in (a)), c) Spike-voltage dependent plasticity (pulse width = 380 ms), d) EPSC as triggered by various pulses for the evaluation of minimal energy consumption of the synaptic device. e) Peaks as triggered by 10 presynaptic spikes at different spike rates and f) the plot of postsynaptic current (synaptic weight) as a function of spiking frequency for the demonstration of spike-rate dependent plasticity (SRDP), where synaptic weight was modulated by frequency of presynaptic spikes.

pulse (Fig. 3c); the increase is due to the increased number of accumulated ions and aligned dipoles in the thin film. However, this increase is not linear; it consists of two concurrent trends during spiking: (1) the spike drives the movement of a number of dipoles and ions; (2) The accumulated dipoles and ions tend to spontaneously drift back their equilibrium position in the interval between pulses. The current level increased abruptly in response to the first few pulses, but this increase weakened as the number of incremental pulses increased, because as the gradient of displaced species across the film increases, the tendency to return to the equilibrium position also increases; eventually, equilibrium between the displacement of ionic and dipolar species and their recovery is established. The decay replicates the trend of memory loss in a human brain (Fig. 3d); i.e., $y = bt^{-m}$ [20,21].

Increase in spike duration, i.e. pulse width, increased the current produced (Fig. 4a). This phenomenon is realized by increase in the number of displaced species as pulse duration increases. The trend in current was obvious at spiking duration < 2000 ms, but became gradual at > 2000 ms. The plateau is imposed by the fixed number of mobile bromides. When only small fractions of the dipoles reorient and anions migrate, increased pulse width could increase the number of displaced species. However, after most of the anions had migrated and accumulated, the number of remaining ions was small, and they became increasingly difficult to move, so in this stage an increase in pulse width induced only a small increase in current. Current peaks are affected by both pulse width and pulse amplitude (Fig. 4b). Enhanced spike amplitudes can also cause increase in current (Fig. 4c).

One of the most important features of a natural neural network is its energy efficiency. Biological synapses use 1–10 fJ per synaptic event. Various pulse amplitudes were tested to trigger EPSC of the synaptic device to evaluate its energy consumption (Fig. 4d). Energy consumption $E = PIt$, where P [V] is pulse amplitude, I [A] is triggered current level, and t [s] is pulse width [22]. A 100-mV pulse triggered an EPSC of ~ 20 pA; energy consumption was ~ 100 fJ/synaptic event. A ~ 10 mV pulse triggered a clear EPSC of ~ 2 pA; energy consumption was ~ 10 fJ/synaptic event, which comparable with that of a biological synapse. The effectiveness of the EPSC was confirmed by applying two successive pulses of 10 mV, which caused PPF behavior with the 2nd EPSC peak increased in comparison with the 1st one. Recent years, energy consumption has been reduced to femtojoule level for three-terminal artificial synapses [2,5b], while for two-terminal structure, comparable energy consumption is still desired. Both two-terminal and three-terminal artificial synapses with low-energy consumption and ultrahigh sensitivity is desired in neuromorphic electronics in different types of future applications.

Slight enhancement in current response was observed when thinner CPE-Br thin film of 33.5 nm was used (Fig. S2a,b). However, when the film thickness is further reduced to ~ 24 nm, severe leakage current makes the device not reliable (Fig. S2c,d).

To compare with CPE-Br artificial synapse, chloride-containing CPE (CPE-Cl) and iodide-containing CPE (CPE-I) were also synthesized (Scheme S1, Scheme S2 and 'Supporting Synthesis procedure'), and applied to similar device structures. Sensitivity in the sequence of CPE-Cl > CPE-Br > CPE-I has been shown (Fig. S3). This trend is probably due to the ion size effect. In the case of halides, iodides have larger ion size than bromides, while chlorides have smaller size. Larger ions are relatively less mobile in response to the same external pulses. Temperature also influences the synaptic behavior by affecting ion migration. Weaker current responses could occur due to the restriction of ion migration at lower temperatures (Fig. S4).

Spike timing dependent plasticity (STDP) is an important learning rule that replicates Hebb's postulate "Cells that fire together, wire together" [23,24]. The rule is applicable to a broad range of species, from insects to humans. STDP involves synaptic weight modulation by adjusting the relative timing between presynaptic and postsynaptic spikes, and usually occurs within a critical window of tens of milliseconds. STDP is also an important rule for the construction of neuromorphic electronics. By adjusting the relative timing between presynaptic and postsynaptic spikes, an anti-symmetric STDP window that replicates the biological one has been achieved using a CPE-Br synapse (Fig. S5a,b); the time scale of its STDP window is comparable with those of biological synapses (~ 100 ms). The similar time scale is beneficial to building up interfaces between electronic and biological neural systems.

Spike-rate dependent plasticity (SRDP) is another fundamental rule of synaptic plasticity, and is regarded as an extended form of Hebbian learning, It is believed to underlie learning, associative memory and forgetting [25]. SRDP involves the dependence of synaptic weight on the spike rate of presynaptic spikes. To investigate whether similar behavior exists in CPE-Br -based synapse, ten successive pulses were applied to the same device at different spike rates. Current peaks increased as spiking rates were increased (Fig. 4e,f). The increase is due to suppression of back diffusion of ions and spontaneously recovered dipoles when the interval between pulses is relatively small.

Long-term plasticity is regarded as the maintenance of memory, *i.e.*, the long-term change in synaptic weight that underlays long-term memory. In an artificial synapse, the long-term change in the conductance was measured by the EPSC level at a constant reading bias. In CPE-Br synapses, increase in the number of pulses could cause increase in current, and this increase did not decay (Fig. S6). This current could be 'erased' by applying pulses with opposite polarity. This long-term change in conductance and 'write'/'erase' behaviors are consistent with a resistive switching behavior reported in the previous literature [26]: some semiconducting thin films at thickness around several tens of nanometers could undergo soft breakdown and maintain the state for a long time [26]. When numerous consecutive strong pulses were applied to a CPE-Br synapse, long-term potentiation was formed (Fig. S7). The current decayed only slightly in 10^4 s; in principle, this implies a retention time of > 10 y by extrapolation from the decay trend.

3. Conclusion

In conclusion, we fabricated a conjugated polyelectrolyte (CPE)-based artificial synapse, which emulated important synaptic working principles, and showed great potential for highly sensitive low-energy consuming applications. The excellent synaptic performance originated from (i) an hybrid working mechanism that ensured the realization of both short-term and long-term plasticity in the same device, and (ii) the mobile-ion rich CPE thin film that mediate migration of abundant ions analogous to a synaptic cleft, and allowed ultrahigh sensitivity and ultralow energy consumption of the synaptic device. Development of this type of artificial synapse is an essential progress towards construction of ultrasensitive highly-energy-efficient and soft neuromorphic electronics.

4. Experimental section

4.1. Materials synthesis

CPE-Br was synthesized by following previous reports [27]. The synthetic approach to the neutral precursor of CPE-I, poly[9,9′-bis(6′-iodohexyl)fluorene-*alt*-1,4-phenylene] (FPN-I), involves the Suzuki copolymerization of 2,7-dibromo-9,9-bis(6′-iodohexyl)fluorene [28] and 1,4-phenylenebisboronic ester [27] using $Pd(PPh_3)_4$ in toluene/ K_2CO_3 (2 M in H_2O) at 85 °C for 24 h (yield 81%). The number-average molecular weight (Mn) of the neutral precursor of CPE-Br (FPN-Br) and FPN-I were measured to be 12,000 g/mol (polydispersity index (PDI) = 3.1) and 17,700 g/mol (PDI = 2.3), respectively using gel permeation chromatography (GPC, in *o*-Dichlorobenzene at 80 °C) relative to polystyrene standards. The cationic poly[9,9′-bis[6′-(*N*,*N*,*N*-trimethylammonium)- hexyl]fluorene-*alt*-phenylene] iodide (CPE-I) was obtained by treating FPN-I with a 30% aqueous solution of trimethylamine in THF/methanol for 48 h. Unlike CPE-I, CPE-Cl was prepared by ion-exchange reaction (details see supporting experimental procedures). The ^{1}H NMR and X-ray photoelectron spectroscopy (XPS) data support to confirm the chemical structure of CPEs (Fig. S8).

4.2. Materials and devices

The CPE solution (0.5% in methanol) was spin-coated onto a cleaned $n+$Si wafer, then annealed on a hot plate at 100 °C for 1 h. Then 100-nm-thick circular-shaped Al metal dots with in-plane size of 8.02×10^{-4} cm^2 were deposited though a shadow mask in a thermal evaporator.

4.3. Measurements

AFM images were obtained using a Dimension 3100 microscope (Digital Instruments). High-resolution TEM with EDS wasobtained using a TEM (JEOL JEM-2100FS). All electrical characteristics of the electronic devices were characterized using a Keithley 4200-SCS semiconductor parameter analyzer in a nitrogen-filled glove box. Differential Scanning Calorimetry (DSC) experiments were performed using a DSC-Q2000 (TA Instruments) over a temperature range of −70 to 150 °C with a ramp rate of 10 °C/min. T_g data was taken from the second heating cycle.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science, ICT & Future Planning) (NRF-2016R1A3B1908431). This work was also supported by the Center for Advanced Soft-Electronics funded by the Ministry of Science, ICT and Future Planning as Global Frontier Project (2013M3A6A5073175), and Creative-Pioneering Researchers Program through Seoul National University (SNU). J.L. acknowledges support by the National Science Foundation Graduate Research Fellowship Program by the United States government under Grant No. (DGE-114747).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2018.02.058.

References

[1] a) V.M. Ho, J.-A. Lee, K.C. Martin, Science 334 (2011) 623;
b) L.F. Abbot, W.G. Regehr, Nature 431 (2004) 796.
[2] Y. van de Burgt, E. Lubberman, E.J. Fuller, S.T. Keene, G.C. Faria1, S. Agarwal, M.J. Marinella, A.A. Talin, A. Salleo, Nat. Mater. 16 (2017) 414.
[3] a) S.H. Jo, T. Chang, I. Ebong, B.B. Bhadviya, P. Mazumder, W. Lu, Nano Lett. 10 (2010) 1297;
b) D. Kuzum, R.G.D. Jeyasingh, B. Lee, H.-S.P. Wong, Nano Lett. 12 (2012) 2179;
c) T. Hasegawa, T. Ohno, K. Terabe, T. Tsuruoka, T. Nakayama, J.K. Gimzewski, M. Aono, Adv. Mater. 22 (2010) 1831;
d) A. Chanthbouala, V. Garcia, R.O. Cherifi, K. Bouzehouane, S. Fusil, X. Moya, S. Xavier, H. Yamada, C. Deranlot, N.D. Mathur, M. Bibes, A. Barthélémy, J. Grollier, Nat. Mater. 11 (2012) 860.
[4] a) A.M. Shen, C.-L. Chen, K. Kim, B. Cho, A. Tudor, Y. Chen, ACS Nano 7 (2013) 6117;
b) F. Alibart, S. Pleutin, D. Guérin, C. Novembre, S. Lenfant, K. Lmimouni, C. Gamrat, D. Vuillaume, Adv. Funct. Mater. 20 (2010) 330;
c) C.J. Wan, L.Q. Zhu, Y.H. Liu, P. Feng, Z.P. Liu, H.L. Cao, P. Xiao, Y. Shi, Q. Wan, Adv. Mater. 28 (2016) 3413;
d) Y.H. Liu, L.Q. Zhu, P. Feng, Y. Shi, Q. Wan, Adv. Mater. 27 (2015) 5599;
e) L.Q. Zhu, C.J. Wan, L.Q. Guo, Y. Shi, Q. Wan, Nat. Commun. 5 (2014) 3158.
[5] a) W. Xu, H. Cho, Y.-H. Kim, Y.-T. Kim, C. Wolf, C.-G. Park, T.-W. Lee, Adv. Mater. 28 (2016) 5916;
b) W. Xu, S.-Y. Min, H. Hwang, T.-W. Lee, Sci. Adv. 2 (2016) e1501326.
[6] E.E. Josberger, Y. Deng, W. Sun, R. Kautz, M. Rolandi, Adv. Mater. 26 (2014) 4986.
[7] a) Y.H. Liu, L.Q. Zhu, P. Feng, Y. Shi, Q. Wan, Adv. Mater. 27 (2015) 5599;
b) C.J. Wan, L.Q. Zhu, J.M. Zhou, Y. Shi, Q. Wan, Nanoscale 5 (2013) 10194.
[8] a) S. Li, F. Zeng, C. Chen, H. Liu, G. Tang, S. Gao, C. Song, Y. Lin, F. Pan, D. Guo, J. Mater. Chem. C 1 (2013) 5292;
b) P. Gkoupidenis, N. Schaefer, B. Garlan, G.G. Malliaras, Adv. Mater. 27 (2015) 7176.
[9] M. Liu, B. Li, X. Cui, Biosens. Bioelectron. 47 (2013) 26.
[10] R. Jiang, X. Lu, M. Yang, W. Deng, Q. Fan, W. Huang, Biomacromolecules 14 (2013) 3643.
[11] J.H. Seo, T.-Q. Nguyen, J. Am. Chem. Soc. 130 (2008) 10042.
[12] a) D. Tordera, M. Kuik, Z.D. Rengert, E. Bandiello, H.J. Bolink, G.C. Bazan, T.-Q. Nguyen, J. Am. Chem. Soc. 136 (2014) 8500;
b) R.D. Costa, E. Ortí, H.J. Bolink, F. Monti, G. Accorsi, N. Armaroli, Angew. Chem. Int. Ed. 51 (2012) 8178.
[13] K.-G. Lim, S.M. Park, H.Y. Woo, T.-W. Lee, ChemSusChem 8 (2015) 3062.
[14] K.-G. Lim, S.M. Park, H.Y. Woo, T.-W. Lee, ChemSusChem 8 (2015) (3062-8).
[15] B. Liu, G.C. Bazan, Conjugated Polyelectrolytes: Fundamentals and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013, p. 371.
[16] A. Garcia, R.C. Bakus, P. Zalar, C.V. Hoven, J.Z. Brzezinski, T.-Q. Nguyen, J. Am. Chem. Soc. 133 (2011) 2492.
[17] J. Park, C.V. Hoven, R. Yang, N. Cho, H. Wu, T.-Q. Nguyen, G.C. Bazan, J. Mater. Chem. 19 (2009) 211.
[18] a) H.T.-Y. Yang, G. Gregori, N. Pellet, M. Grtzel, J. Maier, Angew. Chem. 127 (2015) 8016;
b) C.C. Stoumpos, C.D. Malliakas, M.G. Kanatzidis, Inorg. Chem. 52 (2013) 9019.
[19] R.S. Shenoy, G.W. Burr, K. Virwani, B. Jackson, A. Padilla, P. Narayanan, C.T. Rettner, R.M. Shelby, D.S. Bethune, K.V. Raman, M. BrightSky, E. Joseph, P.M. Rice, T. Topuria, A.J. Kellock, B. Kurdi, K. Gopalakrishnan, Semicond. Sci. Technol. 29 (2014) 104005.
[20] a) H. Ebbinghaus, in Memory: A Contribution to Experimental Psychology (eds trans. H.A. Ruger, C.E. Bussenius, Teachers College, Columbia Univ., 1913.
b) S.D. Sala, Forgetting, Psychology Press, 2010
[21] D.C. Rubin, A.E. Wenzel, Psychol. Rev. 103 (1996) 734.
[22] D. Kuzum, S. Yu, H.-S.P. Wong, Nanotechnology 24 (2013) 382001.
[23] N. Caporale, Y. Dan, Annu. Rev. Neurosci. 31 (2008) 25.
[24] Siegrid Löwel, Göttingen University, The exact sentence is: neurons wire together if they fire together, Löwel, S. and Singer, W Science 255 (published January 10, 1992) Selection of Intrinsic Horizontal Connections in the Visual Cortex by Correlated Neuronal Activity, 1992.
[25] Y. Zhang, Z. Zeng, S. Wen, International Joint Conference on Neural Networks (IJCNN), Beijing, 2014, p. 2226.
[26] W.-P. Lin, S.-J. Liu, T. Gong, Q. Zhao, W. Huang, Adv. Mater. 26 (2014) 570.
[27] O.K. Nag, M. Kang, S. Hwang, H. Suh, H.Y. Woo, J. Phys. Chem. B 113 (2009) 5788.
[28] D. Stay, M.C. Lonergan, Macromolecules 46 (2013) 4361.

Wentao Xu received his B.S. from Beijing Normal University, and Ph.D. in Chemical Engineering from POSTECH in February 2012. He has worked as a research associate professor in Pohang University of Science and Technology (POSTECH) and Seoul National University (SNU). His research interests include synapse-emulating electronic devices, nonvolatile memory devices, graphene electronics, and organic field-effect transistors.

Thanh Luan Nguyen received his BS degree in Chemistry from Ho Chi Minh City University of Science, Viet Nam in 2007 and his PhD degree in 2015 from Department of Nanofusion Technology, Pusan National University, Republic of Korea under the supervision of Prof. Han Young Woo. In 2015, he continued to work as a research professor in the Department of Chemistry, Korea University, Seoul, Republic of Korea. His research interests focus on the design and synthesis of organic optoelectronic materials.

Young-Tae Kim is a senior engineer at Samsung Electronics. He received his B.S. (2012) in Material Science and Engineering from Hanyang University (2012) and Ph.D. (2017) in Material Science and Engineering at Pohang University of Science and Technology (POSTECH). His research interests include (1) quantitative and structural characterization of organic-based optoelectronic devices by transmission electron microscopy (TEM) and atom probe tomography (APT), (2) atomic scale analysis through the Cs-corrected TEM for nano-material and electronic devices, and (3) investigation of correlation between micostructure and physical properties in electronic devices through in-situ electron microscopy.

Christoph Wolf received his Ph.D. in Materials Science and Engineering from Pohang University of Science and Technology (POSTECH) in 2017. He is currently working as postdoctoral researcher at the Institute for Basic Science (IBS) Korea in the Center for Quantum Nanoscience (QNS) located at Ewha Womans University, Seoul. His research field is the first-principles description of magnetic phenomena of atoms, clusters and molecules on surfaces with focus on future application of those systems for quantum computing.

Raphael Pfattner graduated in Physics at Graz University of Technology, Austria in 2007. He received his Ph.D. in Materials Science at NANOMOL in the Institute of Materials Science at the Autonomous University in Barcelona, Spain in 2011. After his postdoctoral appointment at Stanford University, CA, in the group of Prof. Z. Bao, he recently joined the Materials Science Institute of Barcelona (ICMAB-CSIC) as a Juan de la Cierva fellow. His current research interest is focused on charge transport physics, organic semiconductors, organic metals, field-effect transistors and sensors.

Jeffrey Lopez is a graduate student in Prof. Zhenan Bao's research group in the Department of Chemical Engineering at Stanford University. His research is focused on the development and characterization of polymer materials for energy storage applications and he is broadly interested in making new materials for electronics and energy devices of all kinds.

Byeong-Gyu Chae started integrated Ph.D. program at 2013 in POSTECH, Korea. He is majoring in microstructural analysis of semiconductors such as memory devices, LEDs and Li-ion batteries. Especially, his research focuses on correlative analysis by using Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT) for obtaining both the structural and compositional information.

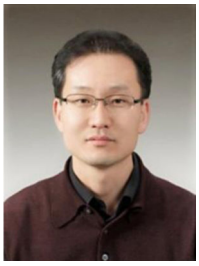
Sung-Il Kim received his B.S. (2017) in Materials Science and Engineering from Korea University, Republic of Korea. He is currently pursuing his integrated Ph.D. in Materials Science and Engineering at Seoul National University (SNU), Republic of Korea. His research interests are focused on organic/inorganic hybrid for synaptic electronic devices, and artificial synapse.

Moo Yeol Lee received his B.S. degree in nanochemistry in 2013, and an M.S. degree in energy engineering in 2015 from the Ulsan National Institute Science and Technology (UNIST). He is currently a Ph.D. candidate at Pohang University of Science and Technology (POSTECH). He is currently interested in advanced organic electronics, especially flexible/stretchable electronics and organic-transistor-based sensors, and their applications in wearable electronics.

Joon Hak Oh is an associate professor in the department of chemical engineering at Pohang University of Science and Technology (POSTECH). He received his Ph.D. degree (2004) from the School of Chemical and Biological Engineering at Seoul National University. He worked on flexible displays as a senior engineer for Samsung Electronics (2004–2006). He then continued his postdoctoral research in the Department of Chemical Engineering at Stanford University (2006–2010). His research interests include organic semiconductors, polymer nanomaterials, organic optoelectronic devices, and carbon nanomaterials.

Hyunsang Hwang received the Ph.D. degree in materials science from the University of Texas at Austin, Austin, Texas, USA, in 1992. He was with LG Semiconductor Corporation for five years. He became a Professor of materials science and engineering with the Gwangju Institute of Science and Technology, Gwangju, South Korea, in 1997. In 2012, he moved to the Materials Science and Engineering Department with Pohang University of Science and Technology, South Korea.

Chan Gyung Park received his Ph.D. in Material Science and Engineering from Northwestern University in 1983. After three years of staff scientist at Oak Ridge National Laboratory, he joined the faculty of Pohang University of Science and Technology (POSTECH) in 1986. He is currently a professor in the Department of Material Science and Engineering at POSTECH and a director for National Institute for Nanotechnology (NINT) in Pohang. His current research interests are nanoscale HREM analyses microscopic phase transformation studies of advanced high-strength low alloy steels, and in-situ straining TEM analysis of super plastic deformation.



Han Young Woo received his Ph.D. degree in Chemistry from the Korea Advanced Institute of Science and Technology (KIAST), Republic of Korea in 1999. After postdoctoral training at the University of California, Santa Barbara (UCSB) in USA, he joined the Pusan National University as an assistant professor. In 2015, he moved to Korea University and he is currently a professor in the Department of Chemistry, Korea University. His current researches focus on conjugated polymers and polyelectrolytes for applications in organic optoelectronic devices, fluorescence chemo- and biosensors.

Tae-Woo Lee is an associate professor in the department of the Materials Science and Engineering at Seoul National University (SNU), Korea. He received his Ph.D. in Chemical Engineering from Korea Advanced Institute of Science and Technology (KAIST), Korea in February 2002. He then joined Bell Laboratories, USA, as a postdoctoral researcher in 2002. From September 2003 to August 2008, he worked in Samsung Advanced Institute of Technology as a member of research staff. He received a prestigious Korea Young Scientist Award from the President of Korea in 2008 and The Scientist of the Month Award from the Ministry of Science, ICT and Future Planning in 2013. His research focuses on printed and organic electronics based on organic and carbon materials for flexible electronics, displays, solid-state lightings, and solar energy conversion devices.