A visible-blind photodetector and artificial optoelectronic synapse using liquid-metal exfoliated ZnO nanosheets

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Abstract

Atomically thin two-dimensional (2D) materials are highly sought for high-performance electronic and optoelectronic devices. Despite being a widely recognized functional material for a plethora of applications, ultra-thin nanosheets of zinc oxide (ZnO) at a millimeter-scale for developing high-performance electronic/optoelectronic devices have not been reported. This has prevented the exploration of electronic and optical properties of ZnO when it is only a few atoms thick. Here, we use a liquid metal exfoliation technique that takes advantage of the van der Waals (vdW) forces between the interfacial oxide and the chosen substrate to obtain ZnO nanosheets with lateral dimensions in the millimeter scale and thickness down to 5 nm. Their suitability for applications is shown by demonstrating a visible-blind photodetector with high figures of merits as compared to their other morphologies. At an extremely low operating bias of 50 mV and low optical intensity of 0.5 mW/cm², our ZnO photodetector demonstrate an external quantum efficiency, responsivity, and detectivity of $4.3 \times 10^3 \%$, 12.64 A.W⁻¹ and $5.81 \times 10^{15}$ Jones at a wavelength of 365 nm. We further utilized the trap-mediated photoresponse in our ZnO nanosheets to demonstrate optoelectronic synapses. Versatile synaptic functions of the nervous systems such as short-term plasticity (STP), long-term plasticity (LTP), paired-pulse facilitation (PPF), spike duration dependant plasticity (SDDP), spike rate dependant plasticity (SRDP), Hebbian spike-time dependant plasticity (STDP) and “learning-experience” behaviors are optically emulated with the ultra-thin ZnO nanosheets. This work presents a new direction to achieve miniaturized high-performance optoelectronic devices based on ZnO that would facilitate the development of photodetectors, artificial intelligence, and optically driven neuromorphics.
**Introduction**

Isolation of graphene by Novoselov et al. has aroused extensive interest in achieving 2D semiconductor counterparts due to their intriguing electronic and optoelectronic properties[1]. In particular, thin layers of 2D materials have gained significant attention in the field of optoelectronics as they offer unique advantages such as strong quantum confinement effects that offer novel electrical, electronic, and optical properties that are distinct from their bulk counterparts along with mechanical flexibility and high compatibility with state-of-the-art silicon-based platform[2-4].

Among prominently studied materials in the last few decades is zinc oxide (ZnO), a highly versatile tunable material[5]. The optoelectronic properties of ZnO in various morphologies have been investigated widely[6]. Due to its strong absorption in the UV region, ZnO is an attractive candidate for visible-blind photodetectors[7]. With a wide bandgap of 3.39 eV, exciton binding energy as large as 60 meV at room temperature, and the ability to undergo a strong quantum confinement effect, atomically thin ZnO promises an excellent platform for optoelectronic applications[8]. Most importantly, oxygen adsorbed onto the surface of ZnO provides low electron densities that can enable low dark current which is ideal for low energy applications[9]. Though thin nanosheets (<20 nm) ZnO has been used as an active layer for various applications, the lack of a reliable and controllable synthesis technique to obtain large area few atoms thin ZnO has prevented the miniaturization of ZnO based optoelectronic devices slowly making the material less competitive compared to other emerging systems relying on atomically thin functional layers[10-12]. Also, ZnO and other planar metal-
semiconductor-metal (MSM) based UV photodetectors developed to date have reported relatively high bias values needed for photon detection (1–20 V) (see Table 1) [13-28]. This is due to the higher recombination rates of photogenerated carriers displayed by MSM photodetectors[29]. To compensate the high operation bias, alternative routes are sought such as adding a dopant to the pristine ZnO, devising a heterostructure or making alterations to the MSM configuration, thereby adding further complications to the synthesis procedure and the fabricated structure[29-31]. As such, it is highly desirable to achieve large aspect ratio ZnO nanosheets with low operational bias in order to open future avenues for this material in the optoelectronics field.

Herein, we have used our recently reported unique and cost-effective liquid metal-based van der Waals (vdW) exfoliation technique[32] to synthesize atomically thin nanosheets of ZnO. Most metals when exposed to air form a thin oxide layer at the metal-air interface in a self-limiting reaction[32-34]. The formed oxide layer is typically only a few nanometres thick, which facilitates the formation of a nanostructure. We utilize the same principle here where atomically thin nanosheets of ZnO with thickness close to 5 nm are obtained with lateral dimensions up to a millimeter scale. The as-synthesized ZnO showed high crystallinity and we demonstrated two key optoelectronic applications in a two-terminal configuration. Firstly, we show a strictly visible-blind UV photodetector, wherein the few atom thick ZnO sheets-based device operated at a low bias of 50 mV, thereby promising low-energy operation compared to other reported similar photodetectors. The developed photodetector addresses some of the technological challenges outlined earlier. The key figures of merit of the photodetector are excellent showing a pathway for miniaturization of ZnO-based devices. Secondly, we have for the first time deployed the two-terminal ultra-thin vdW exfoliated ZnO nanosheet-based optoelectronic device to mimic fundamental synaptic operations. The synaptic device has successfully shown multi-functional utility such as memory transitions, PPF, PPDP, STDP, SRDP, and learning experience behavior from within a single device. The ‘learning-forgetting’ behavior model bears a close resemblance to the behavior of the human brain. Apart from this, we have also emulated the Hebbian synaptic learning and the spatiotemporal dynamic function using a multi-synaptic system. This study, therefore, presents a pathway to miniaturize oxide-based optoelectronics towards monolithic integration on photonics and neuromorphics.

**Results and Discussion**
2D nanosheets of ZnO are acquired using the unique vdW exfoliation technique where a substrate is brought in close contact with the surface of the liquid metal oxide. The method and the materials utilized for the above process are described in detail in the experimental section. It is realized that the non-polar and the monatomic nature of the parent metal provides only weak macroscopic forces between the metal Zn and its interfacial oxide layer[35]. However, the interaction between the solid substrate and the interfacial oxide layer is strong enough which allows the ZnO nanosheets to be lifted off easily leaving behind the liquid metal. This results in clear delamination of the oxide layer on the touched substrate (Figure 1a). Optical images of the transferred ZnO nanosheets onto a pre-cleaned SiO2 substrate are shown in Figure 1b and Note 1 Supporting Information. As seen from the images, this method of exfoliation facilitates the synthesis of nanosheets with a lateral dimension up to a millimeter scale. To characterize the material, a low-resolution transmission electron microscopy (TEM) analysis performed on the as-synthesized ZnO nanosheets is shown in Figure 1c. The technique implemented to transfer the nanosheets directly onto the TEM grids is explained in the experimental section. In-depth microscopy analysis reveals a smooth nanosheet of ZnO, that indicates the relatively thin nature of the material. Careful analysis of the diffraction peaks obtained from selected area electron diffraction (SAED) as shown in Figure 1d yields a lattice d-spacing of 2.8 Å (100) that corresponds to the hexagonal crystal structure. The high-resolution TEM (HRTEM) analysis confirms the unidirectional crystalline growth of the oxide with an inter-planar distance of 2.8 Å that can be indexed to the (100) plane according to the JCPDS #36-1451 (Figure 1e).

The thickness of the synthesized ZnO nanosheets is obtained by atomic force microscopy (AFM) which reveals a thickness of 5 nm (Figure 1f). The stoichiometry of the synthesized oxide layers was analyzed using X-ray photoelectron spectroscopy (XPS) as presented in Figure 1g and h. The binding energies of Zn 2p3/2 and Zn 2p1/2 are located at 1022.24 eV and 1045.32 eV, respectively with separation energy of 23.08 eV[36, 37]. These data support the presence of Zn2+ which also confirms the absence of metallic Zn peak. The O1s spectrum when deconvoluted can be resolved into two peaks positioned at 532.97 eV and 531.41 eV. The peak at 532.97 eV can be assigned to the chemisorbed O or OH- molecules on the outermost surface of the ZnO nanosheet. The contribution from lattice-bound oxygen here becomes indistinguishable from chemisorbed oxygen bounded on the surface of Zn at this resolution due to the atomically thin nature of the nanosheets. Hence the main peak at 532.97 eV can be assigned to the combination of these two oxygen components. This also
explains why the main peak is shifted to a slightly higher binding energy from the bulk position. The small contribution to the peak at 531.41 eV can be assigned to the interstitial oxygen which causes a chemical shift in the metal 2p level due to the absence of a bonded oxygen atom[37, 38].

Figure 1 | Synthesis and characterization of vdW exfoliated ZnO nanosheets (a) Schematic illustration of the vdW exfoliation technique to obtain atomically thin nanosheets of ZnO (b) Optical image of the exfoliated ZnO on a 300 nm thick SiO₂/Si substrate (c) TEM micrograph of as-synthesized ZnO nanosheets (d) SAED pattern of the TEM micrograph. Diffraction spot encircled by green circle corresponds to (100) plane of ZnO
nanosheet (e) HRTEM image of the sample featuring planes (f) AFM topography of the exfoliated ZnO nanosheet (g-h) core-level XPS results of Zn 2p and O 1s.

We analyze the UV-vis-NIR spectra of the as-synthesized ultra-thin ZnO nanosheets to assess their applicability in optoelectronics (Figure 2a). While the absorption cut-off point occurs at around 450 nm, strong absorption is seen in the UV region. The Tauc plot extracted from the absorption spectra reveals an optical direct bandgap of 3.39 eV, which agrees well with the literature[39, 40] (inset of Figure 2a). A deviation from the linear extrapolation curve is observed at the lower energy end between 2.8 eV to 3.1 eV, which reveals a strong density of states (DOS) near the band edge[41, 42]. The XPS valence band (VB) spectrum and the photoelectron spectroscopy in air (PESA) signal measured for the metal oxide is plotted in Note 2, Supporting Information. It is noteworthy that the VB XPS spectrum also shows the presence of defect states in the material. The estimated band structure of 2D vdW exfoliated ZnO nanosheets based on XPS VB, PESA, and Tauc plot are presented in Figure 2b. Typically, trap states in the oxide nanosheets between their energy bandgap arise from the oxygen and/or metal ion vacancies[43, 44]. The existence of these states plays a significant role in the generation and recombination events that occur during the excitation and relaxation processes in a photodetector, respectively[45].

To evaluate the optoelectronic characteristics of ZnO nanosheets, we fabricate source and drain electrodes on the as-synthesized ZnO nanosheets. Figure 2c shows the schematic representation of the two-terminal configuration of our photodetectors with an optical light source illuminating the ZnO nanosheet channel. Figure 2d shows the $I$-$V$ characteristics in the dark and under UV-B and UV-A illumination wavelengths. Inset of Figure 2d shows an optical microscopy image of a representative device subjected to optoelectronic measurements. It is seen that photocurrent in the device ($I_{ds}$) increases remarkably from 1.3 nA in the dark state to 247 nA and 648 nA under the excitation wavelengths of 280 nm and 365 nm, respectively, at 1 V drain-source bias ($V_{ds}$) and illumination intensity of 3 mW/cm². It is to be noted that the device remains unresponsive to wavelengths from visible to NIR.

The normalized transient photoresponse (Figure 2e) shows a relatively higher photocurrent under 365 nm wavelength than 280 nm under identical illumination conditions. The obtained behavior is expected based on the semiconductor bandgap, which results in a photoresponse
constricted only to the UV region. This feature makes our vdW exfoliated ZnO photodetectors extremely suitable for highly selective visible blind UV applications. Power dependant and bias dependant measurements on the same wavelength (365 nm) are shown in Note 3, Supporting Information. Up to three orders of magnitude change in photocurrent are obtained for varying voltage bias between 50 mV and 2 V which indicates the high photodetection capability of ZnO nanosheets.

One of the critical parameters to evaluate the performance of photodetectors is their response speed. Temporal response characteristics of the vdW exfoliated ZnO photodetectors measured under a bias of 50 mV and a light intensity of 3 mW/cm² upon the illumination of 365 nm wavelength are shown in Figure 2f. The rise time (10-90 %) and decay time (90-10 %) are extracted by fitting the rise and decay components with a bi-exponential function

\[ I_{\text{rise}}(t) = I_{\text{dark}}[1 - \exp\left(-\frac{t}{\tau_{\text{rise}}}\right)] \]  

\[ I_{\text{fall}}(t) = I_{\text{dark}} + A\exp\left(-\frac{t}{\tau_{\text{fall1}}}\right) + B\exp\left(-\frac{t}{\tau_{\text{fall2}}}\right) \]  

as specified in Equations 1 and 2\cite{46, 47}.

where A and B are the scaling constants, t is the illumination time, and \( \tau_1 \) and \( \tau_2 \) are the fast and slow decay times of the exponential functions, respectively. The rise time obtained after the single exponential fitting was 11.58 s. The decay characteristics obtained after switching off the 365 nm light source have a fast component of 20.08 s and a slow component of 73.58 s. The presence of double components in the recovery curve is attributed to electron trap states at different levels of trap depths in the semiconductor. Traps in the deeper states take a relatively long time to release the charge carriers leading to a slower response time of the device\cite{48,49}. Thus, the excess lifetime of charge carriers could be one possible reason for the slow decay time of charge carriers.

Additionally, the surface oxygen exchange process also plays a dominant role in the transient response characteristics. Under dark conditions, oxygen adsorbed from the atmosphere extracts free electrons from the exposed surface of ZnO, creating electron depletion zones (Equation 3). Upon illumination at photon energies of and above the ZnO bandgap, electron-hole pairs are generated with holes migrating towards the chemisorbed surface. This action neutralizes the negatively charged surface oxygen ions (Equations 4 and 5). As such, the
concentration of free carriers increases, and the width of the depletion layer decreases. The electrons generated in this process increase the conductivity of the ZnO[26, 50, 51]. This adsorption and desorption phenomenon eventually lead to a relatively slow response time in our vdW exfoliated ZnO.

\[ O_2(g) + e^-(ZnO) \rightarrow O_2^-(adsorbed) \]  
\[ h\nu \rightarrow e^- + h^+ \]  
\[ h^+ + O_2(adsorbed) \rightarrow O_2(g) \]

Figures of merit such as responsivity \((R)\), detectivity \((D^*)\), and external quantum efficiency \((EQE)\) have also been calculated to determine the performance of the ZnO visible-blind photodetectors. The responsivity \(R\), which determines the sensitivity of a photodetector, is calculated as [18]:

\[ R = \frac{\Delta I}{P_{inc} \times A} \]  

where \(\Delta I\) is the difference between photoexcited current and dark current (i.e., \(I_{illumination} - I_{dark}\)), \(P_{inc}\) is the power intensity for a particular wavelength, and \(A\) is the effective illumination area. \(R\) at an illumination intensity of 0.5 mW/cm\(^2\) and voltage bias of 50 mV at a wavelength of 365 nm is calculated to be 12.64 A.W\(^{-1}\) (Figure 2g). The responsivity spectrum reveals a very low sensitivity above the cut-off wavelength and shows a notable increase in response when the excitation energy nears \(\sim3.4\) eV, close to the semiconductor bandgap. These results are consistent with the obtained absorbance spectra (Figure 2a). The responsivity values for various illumination intensities (inset of Figure 2g) reveal a decreasing trend with increasing power intensities. Usually, charges stored in the trap states lead to the recombination and re-emission of carriers. However, those charges stored in the deep sites are not recombined easily, thereby showing a sub-linear dependence of photocurrent[19, 52]. The dependence is demonstrated by fitting the experimental data with the following equation[53] \(R \propto P_{\lambda}^{\alpha-1}\)

Value of \(\alpha\) is obtained as 0.32 which indicates the complex process of electron-hole generation and recombination and reaffirming the existence of trap states in our photodetector[54].
Specific detectivity ($D^*$) represents the detection capacity to detect signals at their lowest power\[55\].

$D^*$ is calculated from the formula\[56\];

$$
D^* = \frac{R_\lambda \sqrt{A}}{\sqrt{2eI_{DARK}}}
$$

(8)

where $R_\lambda$ is the responsivity for a wavelength, $A$ is the effective area of the material subjected to illumination, $e$ is the electronic charge, and $I_{DARK}$ is the current obtained from the device without any illumination. A maximum $D^*$ of $5.81 \times 10^{15}$ Jones is calculated for an applied bias of 50 mV and an intensity of 0.5 mW/cm$^2$ (Figure 2h).

External Quantum Efficiency ($EQE$), another factor to quantify the figures of merit of a photodetector, is expressed as \[57\]

$$
EQE = \frac{h \times c \times R_\lambda}{e \times \lambda}
$$

(9)

where $h$ is the Plank’s constant, $c$ is the velocity of light, $R$ is the responsivity at a wavelength, $e$ is the charge of an electron, and $\lambda$ is the incident light wavelength. A maximum $EQE$ value calculated for the wavelength of 365 nm is $4.3 \times 10^3$ % at an illumination intensity of 0.5 mW/cm$^2$ and a bias of 50 mV (Figure 2i).

From the inset of Figure 2g and figures 2h-i, we see that $R$, $D^*$, and $EQE$ decrease with increasing illumination intensities which can be attributed to the trap states and the surface recombination effect. Usually, in the dark state, the electron density and the dark current are decreased due to electron adsorption into the trap states. This effect is more pronounced here due to the large surface-to-volume ratio of the ZnO nanosheets. At low illumination intensities, the photoinduced holes migrate towards the surface, which combines with the $O_2^-$ and discharge the oxygen adsorbed onto the surface. The absence of trapped holes decreases the recombination rate, thereby prolonging the lifetime of electrons, ultimately leading to an enhanced responsivity. Also, the remaining electrons contribute to a significant photocurrent. Other than this, the short electrode separation of the device (5 μm) allows for a reduced transit time for the charge carriers to be collected in the drain terminal, which eventually enhances the value of EQE\[58\]. Internal gain or photoconductive gain is also feasible when the recombination rate is reduced, and charge carriers can travel through the external circuit.
more than once before getting recombined with their counterpart[14, 46, 59, 60]. All these factors significantly enhance the figures of merit at low illumination intensities. At higher intensities, the saturation of the unoccupied trap states occurs, increasing the recombination of electron-hole pairs, and eventually causing saturation in photoresponse[55, 61, 62]. Values of $R$, $D^*$, and EQE for increasing voltage bias are shown in Note 4, Supporting Information, where we notice increasing values of figures of merit for increasing voltage biases. A comparison of the figures of merit with state-of-the-art UV photodetectors shows the superior performance of our vdW exfoliated ZnO photodetectors as highlighted in Table 1.

It should also be noted that the obtained values are higher than ZnO photodetectors based on other morphologies developed to date. This can be ascribed to the higher surface-to-volume ratio in the 2D form that aids a superior photoconduction behavior compared to bulk counterparts [29, 30, 63, 64]. As a result, the superior R and EQE are obtained for the fabricated 2D-based vdW exfoliated ZnO devices.
Figure 2 | Optoelectronic and photodetection properties of vdW exfoliated ZnO nanosheets
(a) The UV-vis-NIR spectra of as-synthesized ZnO nanosheets. Inset: Tauc plot extracted from the absorption spectrum which reveals a direct bandgap of 3.39 eV (b) Band structure illustration of ZnO nanosheets with the assessed conduction band minimum ($C_{B_{min}}$), valence band maximum ($V_{B_{max}}$), Fermi level and bandgap (c) Schematic of the 2D vdW exfoliated ZnO photodetector (d) The $IV$ characteristics of the device under dark and UV illumination with $P_{inc}$ of 3 mW/cm$^2$. Inset: Optical microscopy image of the tested device (e) Time-resolved photoresponse of the device when subjected to UV illumination at a low bias of 50 mV and an intensity of 3 mW/cm$^2$. (f) Response time of the photodetector under 365 nm illumination calculated at a $V_{bias}$ of 50 mV and power intensity of 3 mW/cm$^2$. (g) $R$ plotted against wavelengths from UV-B to NIR obtained at a bias of 50 mV and an intensity of 3 mW/cm$^2$. Inset: $R$ as a measure of varying intensities at an illumination intensity of 3 mW/cm$^2$ when subjected to 365 nm radiation (h) $D^*$ as a measure of varying intensities (i) $EQE$ measured for different intensities at a bias of 50 mV and an intensity of 3 mW/cm$^2$. 

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We demonstrate another application of our ultra-thin ZnO nanosheets. As synaptic activities can be well-simulated through optoelectronic signals, several 2D materials have been explored to mimic the synaptic functions of the human brain[65, 66]. vdW exfoliated nanosheets of ZnO reveal properties that can be utilized to mimic the fundamental synaptic functions of neurons. Charge carriers in ZnO produce synaptic spikes that replicate the optical excitatory response of the human brain when excited under a 365 nm light source. Figures 3a and 3b show a schematic representation of a biological synapse and ZnO artificial synapse, respectively. In a biological neural network, the connection between a presynaptic axon and a postsynaptic dendrite through the synaptic cleft forms a synapse. Upon an action potential, neurotransmitters released from the presynaptic neurons transfer to the synaptic cleft. Following this, receptors of postsynaptic neurons bind together to receive the transmitted information from the synaptic cleft. This process creates a conductive channel for signal transmission between neurons and leads to cognitive functions in a neural network[67, 68]. The persistent photocurrent (PPC) exhibited by our ZnO photodetectors under the illumination of 365 nm can be harnessed to mimic several synaptic functions as discussed in the following sections.

At any given time, perceptual organs receive both frequent and sporadic information from the surrounding environment, which is registered in the human sensory memory (SM)[69, 70]. Information received with attention is transmuted into short-term memory (STM). Under frequent maintenance, the same information can be converted into long-term memory (LTM)[71]. This combination of STM and LTM facilitates the learning and forgetting process in the human brain[72, 73]. In an artificial optoelectronic synaptic device, change in conductance (referred to as synaptic weight)[74] helps comprehend key cognitive abilities such as self-learning, forgetting, and memory[66, 75, 76]. The process referred to as synaptic plasticity can be categorized into short-term and long-term potentiation (STP and LTP) which corresponds to the short and long-term memory (STM and LTM) of the human brain[77, 78]. STP is a temporary potentiation of neuronal activities that lasts only for a few minutes or less, whereas LTP is a permanent potentiation that lasts from hours to years[71, 79].

Since communication in neurons usually occurs by transmitting data in the form of electrical and electrochemical signals in the range of few tens of milli-volts[80], a bias voltage as small as 50 mV is applied in our vdW exfoliated ZnO synaptic device. Both LTP and STP are associated with rehearsal - stimulation frequency, which is well-replicated in our few atom
thick ZnO optoelectronic synapse[81]. Exposing the device to a light intensity of 3 mW/cm² and using a short pulse width of 0.5 s indulges the postsynaptic current (PSC)[82], which rapidly increases from 9.9 nA to 30.8 nA (Figure 3c). In the absence of light, however, PSC decays gradually to its original state, thereby displaying the sensory memory behavior in the biological synaptic potential[83].

Like biological synapses, our ZnO devices exhibit stimulation frequency-dependent learning[84]. For instance, exposing the device to a frequency of 0.1 Hz under the same light intensity and pulse width over a stimulation period of 50 s shows a further gain in synaptic weight. At the end of the stimulation period, the device displays an increased PSC of 71.4 nA (Figure 3d). While this induces the STP behavior in our artificial synapse, frequent STP maintenance can be converted to LTP[85]. Photonic spikes with the same intensity, pulse width, and stimulation period but with a higher rehearsal stimulation frequency of 0.8 Hz exemplifies an LTM behavior which further increases the PSC to 223.9 nA. Optical spikes with increased PSC take a comparatively longer time to decay than spikes induced by low rehearsal stimulation frequency. Thus, both STP and LTP behaviors can be observed in our devices with strong (LTM) and weak (STM) potentiation effects through varying frequency stimulations. As such, our devices follow the Atkinson and Shiffrin human memory model of cognitive learning[86].

Varying frequency stimulation behavior observed in our vdW exfoliated ZnO synaptic device can be explained through the mechanism of electron trapping and de-trapping[87, 88]. The adsorbed oxygen molecules on the surface of ZnO act as trap sites and play a pivotal role in the charge transfer process which facilitates the learning behavior in our artificial synapse[89]. As depicted in Figure 3e, when a single short optical pulse is illuminated, as in the case of SM, trapped electrons that are swept off the defect sites fail to stay for an extended period in the conduction band due to a long time interval before the arrival of the next spike[87]. At low stimulation rates, the time interval between consecutive optical spikes becomes relatively shorter which causes a gradual accumulation of charge carriers in the conduction band. This reduces the time for charge carriers to diffuse back to their original states and facilitates the transportation of electrons to the drain terminal, which improves the channel conductance. This effect could last for a few seconds and mimics STM behaviour of the human brain. At high stimulation rate, photoinduced electrons do not have enough time to diffuse back. As a result, the device shows a predominant increase in channel conductance.
which decays slowly and lasts from minutes to hours. As such, emulating LTM behaviour of a neural network[88].

Strong and weak potentiation effects can also be obtained by applying strong and weak photonic pulses[90, 91]. Here, LTP is identified as a time-dependant paradigm that can be classified into early-form LTP and late-form LTP[91]. An early-form LTP describes the fading of memory over time, while the late-form LTP defines a stabilized memory – where no visible change is observed in the synaptic weight [92]. Figure 3f shows the PSC obtained under the influence of two different light intensities, i.e., 8 mW/cm$^2$ and 11 mW/cm$^2$. It is observed that the attained variation in synaptic plasticity is proportional to the power intensity of the illuminating source. When a photonic pulse with an intensity of 8 mW/cm$^2$ is exposed to the device, PSC with an amplitude of ~93.2 nA is measured. However, when a light pulse with a stronger intensity of 11 mW/cm$^2$ is applied to the device, it induces a PSC of 195.6 nA with a larger synaptic weight change than 8 mW/cm$^2$. Closer observations reveal that PSC induced by a lower light intensity attains its late-form LTP at an earlier period (at nearly 3280 s) and remains in its form till 7000 s, where it reaches the initial current level of ~3.5 nA. On the other hand, PSC produced by a higher light intensity decays gradually and attains its late-form LTP at a later period of 4400 s. The current of 8.2 nA obtained after the retention period is seen to be slightly higher than the dark current (~3.5 nA). These results indicate that memory formed with spikes of higher intensities can be retained for a longer period, thereby replicating the LTM behaviour of the brain. Also, the ability to retain data for more than 3000 s specifies the high retention capacity of our synaptic device.
Figure 3 | Potentiation effects of ZnO synaptic device (a) Pictorial representation of the biological synapse structure (b) Schematic of ZnO artificial optoelectronic synapse (c) Optical imitation of sensory memory at an intensity of 3 mW/cm² and a pulse width of 0.5 s (d) Replication of STM and transition to LTM induced as a result of increasing frequency stimulation at an excitation wavelength of 365 nm with a 0.5 s pulse width and at a pulse intensity of 3 mW/cm² (e) Band structures depicting the mechanism of charge trapping/de-trapping to emulate the STP and LTP phenomena (f) PSC obtained due to strong and weak photonic pulses. The upper panel shows PSC induced by a single photonic pulse with an intensity of 8 mW/cm² and a pulse width of 0.5 s. The lower panel records a PSC excited at a power intensity of 11 mW/cm² and a pulse width of 0.5 s.

Spike-duration-dependant-plasticity (SDDP), one of the crucial concepts in neuroscience, facilitates the intellectual process of learning and forgetting[21, 93]. Here, the process of learning has been impersonated by inducing an excitatory postsynaptic current (EPSC)[94]. Under the influence of 365 nm optical stimulus, the ZnO artificial optoelectronic device was exposed to varying spike durations (t) of optical pulses that exhibit an excitatory synaptic response (Figure 4a). Change in EPSC (ΔEPSC) for varying pulse durations plotted in the...
inset of Figure 4a reveals an increasing amplitude for increasing spike duration. Longer (shorter) spike duration induces a higher (lower) photocurrent due to an increased (reduced) generation of photocarriers[83]. The synaptic weight varies depending on the photocurrent generated for a particular spike duration. The attained phenomenon emulates the excitatory biological response. The psychological learning process is initiated by providing a train of identical presynaptic optical pulses to attain excitatory rehearsal stimulations[95]. By applying 150 consecutive optical pulses, at a fixed pulse width and light intensity of 0.5 s and 3 mW/cm², our ZnO artificial synapse shows an increasing EPSC for a growing number of pulses, thereupon signifying a synaptic potentiation response (Figure 4b). When exposed to varying voltages (i.e., 20, 50, and 100 mV, respectively), the device displays a higher EPSC amplitude at higher biases. Irrespective of the bias voltage, faster learning is observed for the initial set of spikes, which gradually saturates with increasing spike numbers. This implicates the need for a lesser number of rehearsal stimulations to retain memory while going through a continuous learning process[96]. The EPSC decay characteristics obtained after the application of 150 pulses are plotted in Figure 4c. Regardless of the bias voltage, retention characteristics reveal those charge carriers always self-decay to their original state. Higher bias, however, provokes charge carriers to recombine at a slower rate which prolongs their decay time. Values obtained from the fitting data[88] mentioned in Table S1 reveal that τ₁ and τ₂ have different time scales where τ₂ is at least one order of magnitude higher than τ₁. The difference in value helps to define the STM and LTM states in the decay process. With an increasing number of identical spikes illuminated on the device, a higher ΔEPSC with a slower decay and a longer retention time is observed (Note 5, Supporting Information).
The LTP characteristics and translation of STM to LTM are further demonstrated by pulsing the artificial synaptic devices with photonic pulses of different intensities. A dark current of \(~4.9\) nA is measured for a representative ZnO synaptic device which increases to \(6.6\) nA after the device is illuminated with an optical pulse of \(1\ \text{mW/cm}^2\) intensity and recovery time of \(1000\) s (Figure 4d). By applying consecutive photonic pulses with increasing light intensities, increasing values of dark currents are measured at the end of every retention cycle (\(i.e.,\) 10.10, 14.34, 17.96 nA for 3, 5, and 7 mW/cm\(^2\) respectively). This cumulative modulation with light pulses depicts a vivid transformation of memory retention from STM to LTM state.

Paired pulse facilitation (PPF), is also an important phenomenon in neurophysiology that helps decipher temporal information such as visual and aural signals[97]. When two excitatory presynaptic spikes of the same pulse width are applied in sequence, the attained postsynaptic weight depends heavily on the time interval between synaptic pulses. In principle, a smaller (larger) time interval leads to a larger (smaller) EPSC upon the excitation of the second spike. Figure 4e mimics the PPF phenomenon of two identical excitatory optical pulses obtained by inducing a smaller time interval \((\Delta t)\) of 0.5 s. Here, the photocurrent obtained by the second optical pulse \((A_2)\) is higher than that of the first optical pulse \((A_1)\). The PPF index ratio \((A_2/A_1)\), measured between the amplitude of the second spike and the first spike is extracted and plotted as a function of time interval in Figure 4f.
In a biological neural network, the residual effects of Ca$^{2+}$ triggered by the excitation of the first spike cause an overall enhancement of Ca$^{2+}$ concentration after the pulsation of the second optical spike. With increasing time intervals, a gradual decay in the residual content of Ca$^{2+}$ is caused after the excitation of the first spike, which results in a lesser change in EPSC[97]. Analogous to the Ca$^{2+}$ concentration in the biological synapse, PPF of an artificial optoelectronic synapse can be elucidated with the relaxation time of photogenerated carriers. Electron-hole pairs generated by the first optical pulse undergo a smaller relaxation time if a second optical pulse is excited within a shorter time interval. As such, causing an enhancement in EPSC. At time intervals larger than the relaxation time, the magnitude of photoresponse of the second optical spike becomes like that of the first spike due to the complete diffusion of carriers to their original state. Thus, paired pulses with shorter time intervals generate a higher PPF due to carrier augmentation, whereas excitatory pulses induced with a longer time interval show no improvement in EPSC by displaying a lower PPF that saturates at a value closer to 120 %. PPF phenomenon can also be applied in the areas of temporal-frequency filtering[98] as shown in Note 6, Supporting Information.

Spike-rate-dependent plasticity (SRDP), is also mimicked by our vdW exfoliated ZnO synaptic devices[99]. The variation in the time interval between photonic pulses enables a transition from paired-pulse facilitation (PPF) to paired-pulse depression (PPD)[90] (Figure 4g). To enable this conversion, the initial set of stimulations were subjected to a stimulation frequency of 0.67 Hz (Figure 4h). Near saturation is observed within 350 s with a 216 nA of EPSC. As a subsequent step, when the device is subjected to photonic pulses with an increased time interval of 0.1 Hz, it reduces the EPSC to 114 nA in its steady-state enabling a facilitation-depression transition (Figure 4i). This conversion can be explained in the terms of charge trapping/de-trapping mechanism in ZnO nanosheets discussed earlier[90].
A proof-of-concept “learning-experience” is demonstrated in our ZnO artificial optoelectronic synapses, as shown in Figure 4j. A noticeable increase in synaptic weight is observed within 31 pulses and then decayed spontaneously to a transitional state in the train interval. This can be related to the learning-forgetting phenomenon that occurs in the human brain where learned information can be forgotten over time. After which, the decayed synaptic weight is recovered within 11 pulses during the second stimulation (relearning) process to obtain an identical potentiation of synaptic weight. This is almost half of the 21 pulses that were required for the first stimulation process. These behaviors resemble the learning-forgetting process of the human brain, where stimulating the brain frequently requires very little time to relearn the lost information, and by doing so strengthens the memory permanency. Similarly, we also demonstrate “learning-experience” using identical spikes of different frequencies (see Note 7, Supporting Information).
Figure 4 | Optical stimulation of synaptic functions in ZnO artificial optoelectronic synapse obtained at a 365 nm illumination wavelength (a) Transient PSC of ZnO artificial synapse emulating EPSC at a fixed intensity of 3 mW/cm² (b) EPSC obtained for identical spiking intervals when subjected to various voltage bias (c) EPSC self-decay characteristics obtained after 150 times of identical spiking. The data is fitted using double-tailed exponential decay function (d) EPSCs obtained by exciting photonic pulses under varying intensities (e) The PPF phenomenon characteristics extracted from the device by applying two identical spikes with a pulse width of 0.5 s and a time interval (Δt) of 0.5 s at a power intensity of 3 mW/cm² (f) PPF index as a function of...
the time interval between pulses at a power intensity of 3 mW/cm² (g) PPF to PPD conversion obtained by altering the time interval between pulses (h) PPF obtained at a time interval of 1 s and a pulse width of 0.5 s (i) PPD obtained at a pulse width of 0.5 s and an increasing time interval of 10 s (j) Imitation of the “learning-experience” behavior of the human brain obtained at a pulse width of 0.5 s. The frequency applied to obtain the behavior is 0.18 Hz.

Formulating a multi-synaptic system is also an essential part of a synaptic network[100]. Triggering two or more synaptic pulses in a spatial or temporal mode heavily depends on the number of pulses and the time interval between two consecutive pulses. This facilitates formulating a spatiotemporal dynamic function by assimilating multiple synaptic neural networks[101]. In a bid to realize a spatiotemporal logic in our vdW exfoliated ZnO nanosheets, two devices referred to as “presynapse 1” and “presynapse 2” are configured as depicted in Figure 5a. Light sources of 280 nm and 365 nm wavelength were illuminated on the presynapse 1 and presynapse 2 devices, respectively.

Initially, when the device is irradiated with a 280 nm wavelength to invoke presynapse 1 with a pulse width of 0.5 s and intensity of 3 mW/cm², a change in PSC is observed[65]. Under the same testing conditions, exciting the synaptic device with a 365 nm light source (presynapse 2) induces a 74.31 % larger ∆PSC₂ when compared to ∆PSC₁ (Figure 5b). The obtained higher change in magnitude of PSC₂ attributes to the bandgap of ZnO semiconductor.

Concurrent triggering of presynapse 1 and presynapse 2 causes the photo-generated carriers by the second optical spike to be added to the photocarriers of the first optical spike which results in a maximum change in the magnitude of PSC. This spatiotemporal change can however be altered by varying the time interval between the spikes. So, when ∆tₜₚₑᵣₑ₂₋ᵣₑ₁ = 0, the net value measured at the trailing edge of the second optical pulse is 151.53 % and 225.84 % greater than the values induced by ∆PSC₁ and ∆PSC₂, respectively. Increasing the |∆tₜₚₑᵣₑ₂₋ᵣₑ₁| however, decreases the value of PSC asymmetrically due to the difference in change in PSC induced by presynapse 1 and presynapse 2 (shown in Figure 5c).

To demonstrate interactive associative learning[102], Pavlov’s classical conditioning experiment[103] was depicted with our vdW exfoliated ZnO nanosheets. Here, neutral and conditioned stimuli were initiated by illuminating the 280 nm light source, and an unconditioned stimulus was introduced by using the 365 nm light source. The initial phase of bell ringing which is considered as a neutral stimulus is obtained by illuminating the device with 6 consecutive pulses (pulse width of 0.5 s and power intensity of 3 mW/cm²) of 280 nm
wavelength source. This induces a PSC of 121.1 nA. The conditioning/training phase which involves the application of both neutral and unconditioned stimuli provides a maximum PSC of 278.9 nA. It is seen that the neutral stimulus initiated by only bell ringing produces PSC which is lesser than the threshold value set at 140 nA for a conditioned salivation response. After the conditioning phase, the conditioned stimulus of bell ringing results in PSC with an amplitude of 163.7 nA which is more than the threshold value (140 nA), as depicted in Figure 5d. PSC obtained above the threshold value upon the illumination of 280 nm wavelength can be associated with an increase in the number of charge carriers after the conditioning cycle. As such, the generation of a higher PSC value than the set threshold after conditioning/training cycles mimics Pavlov’s conditioning theory in our ZnO devices.

The ability for a neuron to learn and re-learn a task has been made possible by simultaneous and repeated activation between their connections. This is referred to as the Hebbian learning process[104] where the synaptic weight between the presynaptic and postsynaptic neurons can be altered by controlling the activation timing between the interconnected neurons. This learning process initiated through spike-time-dependent-plasticity (STDP)[105] is also emulated by our vdW exfoliated ZnO devices. A setup similar to Figure 5a with the same devices was used this time, however, one of the devices was referred to as a presynaptic neuron and the other one as a postsynaptic neuron (Figure 5e). By illuminating both the devices with a 365 nm wavelength source, the pulse width of 0.5 s, and power intensity of 3 mW/cm², a symmetric STDP is obtained by varying the time interval between presynaptic spikes and postsynaptic spikes. The synaptic weight as a function of $\Delta t_{\text{post-pre}}$ defined as

$$\Delta PSC = \frac{(PSC_{\text{post}} - \Delta PSC_{\text{pre}})}{\Delta PSC_{\text{pre}}}$$

is plotted in (Figure 5f). Irrespective of the order in which the pre and postsynaptic spikes were stimulated, a symmetric change in synaptic weight is obtained. Similar to Figure 5c, $\Delta PSC$ is maximum when $|\Delta t_{\text{post-pre}}|$ has the least value and symmetrically decreases with increasing $|\Delta t_{\text{post-pre}}|$. Though an array of devices is necessary for large-scale neuromorphic computation, this demonstration shows that our ZnO-based multi-synaptic network can mimic the fundamental behavior of Hebbian learning. Table 2 summarizes various state-of-the-art synaptic devices and their synaptic functions which have been emulated successfully. Energy consumption is one of the critical parameters that determine the potential of an artificial synapse network[78]. The optical energy ($E_{\text{opt}}$) for a single pulse event can be calculated using the formula $E_{\text{opt}} = P \times t \times S$ [106], where $P$ is the illumination power applied for an optical spike with time duration $t$ and $S$ is the active area of
the device. Under the excitation wavelength of 365 nm, with a pulse width of 70 ms, the illumination intensity of 0.5 mW/cm², and an active area of 250 μm², the energy consumption of our device is obtained as 87.5 pJ. Though this value is higher than the energy consumption of a biological synapse (~10 fJ per event), it can be brought down by reducing the spike width and the active area of the device. For instance, if the active area of the device can be scaled down by using the electron beam lithography technique (~ 0.02 μm²), the energy consumption of our ZnO artificial synaptic device is projected to be 7 fJ.

Figure 5 | Interactive associative learning and Hebbian learning emulated by ZnO artificial synaptic device (a) Schematic of two ZnO synaptic devices configured to represent multi neural system using 280 nm
and 365 nm stimuli that represent presynapse 1 and presynapse 2, respectively (b) Temporal PSC obtained by applying single or a pair of spatiotemporally correlated presynaptic optical pulses (c) Change in PSC as a function of the time interval between optical stimulations when excited at presynapse 1 and presynapse 2 (d) Classical conditioning demonstrated by Pavlov’s dog experiment using 280 nm and 365 nm as neutral/conditioned and unconditioned stimuli. A pulse width of 500 ms and a light intensity of 3 mW/cm$^2$ was used to obtain the transient PSC. The blue dotted line indicates the threshold value set at 140 nA. After training, the conditioned stimulus produced an effective response with a PSC of 163.7 nA (23 nA more than the threshold value) (e) Pictorial illustration of two ZnO synaptic devices configured to mimic STDP by using optical pulses of 365 nm (f) ∆PSC as a function of the time difference between pre and postsynaptic pulses.

Conclusions

A facile method has been used to synthesize thin nanosheets of ZnO by exploiting the vdW forces that naturally occur between the oxide surface and any given substrate. This controllable synthesis process aids in attaining wafer-scale nanosheets with thicknesses as low as 5 nm. We have demonstrated the usage of vdW exfoliated ZnO nanosheets for dual applications - one as a UV photodetector and an artificial optoelectronic synapse. A distinct visible-blind photoresponse was obtained at a bias voltage as low as 50 mV, with high figures of merits. The slow response speed, which corresponds to a persistent photocurrent, has been utilized in devising a biomimetic photonic synaptic device. Important behaviors such as STP and LTP memory retention characteristics, learning-experience, STDP, SDDP, SRDP, and interactive associative learning modulated through optical signals have all been demonstrated to replicate the synaptic connectivity of the human brain. The realization of such low power consuming photodetectors and artificial synapses could aid in devising neuromorphic systems for future optoelectronic synaptic neural systems.

Experimental Section

Synthesis of 2D ZnO nanosheets – 2D ZnO nanosheets was synthesized via a liquid metal vdW exfoliation technique inside a glovebox that is continuously purged with N$_2$ gas. A molten state of pure zinc metal (99.8 %, Roto Metals) was obtained by placing the metal on a microscopy glass slide and using a hot plate heated to 500 °C. This chosen temperature facilitated the melting of zinc (which occurs at 420°C) and assisted in the interfacial reaction of the metal with atmospheric oxygen. A self-limiting Cabrera-Mott reaction occurs which forms an oxide layer on the outer surface of molten zinc. The metal in its molten state which
appears dark grey at the first sight was subjected to preconditioning to remove the pre-existing thick oxide layer, and to expose only the pristine metal surface. Pre-conditioning of the liquid metal in an oxygen-controlled atmosphere was achieved by placing the molten zinc in between heated microscopy glass slides. By doing so, we observed that the pristine zinc droplet penetrated through the native oxide layer and oozed out in a squeezing motion due to the pressure applied by touching the top surface of the liquid metal with the piece of a heated glass slide.

After preconditioning, the freshly formed interfacial oxide layer that appears on top of the liquid metal’s surface was exfoliated by touching the liquid metal with suitable substrates such as SiO₂, glass, fused silica, and TEM grids. Before touch printing, rigid substrates were preheated to 500 °C to avoid thermal shock and freezing of the molten metal upon interaction. TEM grids were placed on soft PDMS for oxide transfer to avoid smashing the fragile grids. Electrodes were fabricated using the standard photolithography process. The metal electrodes made of Cr/Au (10/100 nm) were deposited by electron-beam evaporation, followed by lift-off in acetone to obtain the required metallic contact pads for electrical measurements.

Characterization - Optical microscopy images of ZnO nanosheets were taken with the help of a Leica optical microscope. AFM was conducted using the Bruker Dimension Icon AFM to analyze the morphology of ZnO nanosheets. AFM images were analyzed using the Gwyddion 2.36 software. X-ray photoelectron spectroscopy (XPS) was carried out through a Thermo Scientific K-Alpha XPS spectrometer with a base pressure of <1×10⁻⁹ mbar and featuring a monochromatic Al Kα X-Ray source (hv = 1486.7 eV) and a concentric hemispherical analyzer operated with a pass energy of 50 eV. All binding energies were referenced to adventitious surface carbon, with the C1s peak at 284.8 eV. PESA measurements were performed using a Riken Kekei AC-2 spectrometer. A power intensity of 50 nW was used for the samples subjected to measurement. UV-vis absorbance measurements were obtained using the CRAIC 20/30 microspectrophotometer. Low and high-resolution TEM images and SAED were obtained JEOL 2100F that operates at 200 keV equipped with Gatan Orius SC1000 CCD camera.

Measurements - All electrical and optical measurements were performed in the ambient atmosphere. Electrical characterization was performed using the Agilent B2912 source meter. For optoelectronic measurements, commercial monochromatic light-emitting diodes (Thorlabs, Inc.) with wavelengths ranging from 280 to 850 nm were employed as excitation.
sources during the experiments. All measurements were performed in the dark with the illumination of only the target wavelength. The illumination power intensities were calibrated by a commercial power meter photodetector (Newport Corporation). The laser beam was directed vertically onto the nanosheets at a fixed distance of about 1.5 cm from the linkam stage. Pulse width modulation of light sources was facilitated by using the Arduino-Uno programmable microcontroller board.

Acknowledgments

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Table 1. Comparison of the figures of merit of semiconductor-based UV photodetectors (NM: Not Mentioned)

<table>
<thead>
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<th>Materials</th>
<th>$\lambda$ (nm)</th>
<th>Thickness (nm)</th>
<th>$P_{\text{inc}}$ (mW/cm$^2$)</th>
<th>$V_{\text{bi}}$ (V)</th>
<th>Area ($\mu$m$^2$)</th>
<th>$R$ (A/W)</th>
<th>$D^*$ (Jones)</th>
<th>EQE (%)</th>
<th>Response time (s)</th>
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<td>Cds nanowires</td>
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<td>110</td>
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<td>1</td>
<td>3×10⁻²</td>
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<td>2.3×10⁻¹</td>
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Table 2. State-of-the-art artificial synaptic devices

<table>
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<tr>
<th>Active layer</th>
<th>Synapse type</th>
<th>λ (nm)</th>
<th>$P_{\text{inc}}$ (mW/cm$^2$)</th>
<th>Presynaptic spike width (ms)</th>
<th>PP (%)</th>
<th>Synaptic functions</th>
<th>Reference</th>
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<tr>
<td>ZnO nanorod</td>
<td>Optical</td>
<td>36.5</td>
<td>3</td>
<td>500</td>
<td>17.0</td>
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<td>37.0</td>
<td>40</td>
<td>18.28</td>
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<td>Ga$_2$O$_3$ film</td>
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<td>25.4</td>
<td>260</td>
<td>1.3</td>
<td>10</td>
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<td>ZnO film</td>
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<td>36.0</td>
<td>2000</td>
<td>NM</td>
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<td>&gt;5×10$^3$</td>
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* The size of the ZnO nanosheet varies between 3 – 30 μm
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<th>Material</th>
<th>Property</th>
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<th>Value</th>
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<td>InGaZnO</td>
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<td>-</td>
<td>100</td>
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<td>La&lt;sub&gt;1.875&lt;/sub&gt;Sr&lt;sub&gt;0.125&lt;/sub&gt;NiO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>36</td>
<td>5</td>
<td>220</td>
<td>5000</td>
<td>~1 38</td>
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<td>V</td>
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<td>~1 90</td>
<td>Yes</td>
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<td>No</td>
<td>Yes</td>
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References


68. Sütő, T. C., Neuron 2018, 100 (2), 276-293.
70. Han, H.; Yu, H.; Wei, H.; Gong, J.; Xu, W., Small 2019, 15 (32), 1900695.
Liquid metal exfoliated ZnO nanosheets provide a simple yet effective platform to demonstrate two key optoelectronic applications in a two-terminal configuration—one as a miniaturized UV photodetector and the other as an artificial optoelectronic synapse. By exploiting the trap mediated states in the material, many key cognitive functionalities are emulated solely through optical stimuli.
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Author/s:
Krishnamurthi, V; Ahmed, T; Mohiuddin, M; Zavabeti, A; Pillai, N; McConville, C F; Mahmood, N; Walia, S

Title:
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Date:
2021-08

Citation:

Persistent Link:
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