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ABSTRACT

Memristors characterized by non-volatile memory resistance switching are promising candidates for building brain inspired computing architectures. However, existing memristive devices are still far from the energy efficiency of petalops per joule exhibited by biological neural networks. Therefore, to achieve the goal of ultra-low power operation, it is necessary to develop new materials for the active layer in memristors. Here, we show highly energy efficient memristive devices built from liquid-exfoliated 2D WS\textsubscript{2} and MoS\textsubscript{2} nanosheets, enriched in monolayers using a cascade centrifugation method. Lateral devices with electrochemically inert electrodes were built using the drop casting method. The devices show non-volatile resistive switching with a remarkable low energy consumption. This work contributes to the realization of energy efficient and high performance neuromorphic computing applications.

The data deluge in the digital age and reaching the limits of existing technologies call for the development of new materials and devices for next generation memory and computing technologies. The human brain is based on a non-Von-Neumann computing paradigm, showing an incredible computational power and energy efficiency of petalops per joule. On the other hand, current computational technologies are built using the Von-Neumann architecture, in which memory and processing are separate units, which has become a bottleneck in the processing of big data at high speed and consumes large amounts of energy. Thus, in order to meet the present and future data storage and processing needs, it is necessary to develop new nanoscale non-volatile memory devices with improved performances in terms of speed, endurance, retention, and most importantly power consumption.

Memristive devices, based on emerging two-dimensional (2D) semiconducting materials, are potential candidates for brain inspired computing applications due to their unique properties.\textsuperscript{11-13} Until recently, it was believed that non-volatile switching is not scalable to sub-nanometer size owing to leakage currents, but Ge et al.\textsuperscript{14} demonstrated this effect in monolayer atomic sheets. Memristors are non-volatile memory devices based on resistive switching (RS) effects, with a simple two-terminal structure, three dimensional stacking capability, high flexibility, ease of fabrication, and low cost.\textsuperscript{15-17} Two dimensional (2D) crystals show unexpected properties due to quantum confinement effects, in contrast to their corresponding 3D counterparts. Transition metal dichalcogenides (TMDs)\textsuperscript{18} are a class of 2D materials with the chemical formula MX\textsubscript{2}, where M is a transition metal element from group IV B, V B, or VI B and X is a chalcogen (S, Se, or Te), which have semiconductor properties. TMDC crystals consist of an ordered packing of crystalline layers bound together by weak van der Waals forces, enabling exfoliation using small energies and easy 3D stacking. Each layer is formed by the covalent bonding of atoms in the form X–M–X, with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms.\textsuperscript{19}

Among 2D semiconducting TMDs, MoS\textsubscript{2} and WS\textsubscript{2}, here generically referred to as MX\textsubscript{2}, are seen as attractive candidates for high performance memristive devices due to their distinctive physical and electrical properties.\textsuperscript{7,9} Moreover, these materials are compatible with conventional silicon based technologies.

MoS\textsubscript{2} is the most investigated 2D material after graphene. It has a carrier mobility, which varies significantly (1–1000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}) with temperature, layer number, and synthesis method. It has a high on/off current ratio of \(\approx 10^6\) at room temperature and a single layer bandgap of \(\sim 1.8\) eV, indicating excellent performances for electronic and optoelectronic devices.\textsuperscript{13} WS\textsubscript{2} also has a high ON/OFF current...
ratio of $10^{37}$ and a tunable bandgap of $\sim 2.1$ eV.\textsuperscript{15} The computed electron mobility is very high at 1103 cm$^2$/V-s, which makes it a good candidate for low-power applications.\textsuperscript{19} Many 2D materials used for resistive switching are produced using solution-based methods because initially mechanically exfoliated nanosheets such as MoS$_2$ did not show significant RS behavior.\textsuperscript{1} In addition, solution processing methods allow for an exfoliation with low cost, low defect density, high scalability, and easy integration into electronic devices by spin-coating or drop-casting methods.

Liquid phase exfoliation (LPE) has proved to be a powerful and versatile technique, more than the other liquid exfoliation methodologies, for the large scale production of defect-free 2D nanosheets from a diverse range of layered materials.\textsuperscript{1} LPE consists in the sonication or shearing of the bulk material in a liquid (e.g., solvent, surfactant, or polymeric solutions), which must be appropriately chosen to stabilize the nanosheets against reaggregation. However, the nanosheets obtained have a broad thickness and lateral size distribution and low monolayer content. Therefore, it is necessary to employ another method to solve this issue. Among the various techniques developed, mostly based on centrifugation, liquid cascade centrifugation (LCC) is the most efficient, scalable, versatile, and high-yield.\textsuperscript{21} LCC is based on a set of iterative centrifugation cascades, designed to achieve highly efficient nanosheet size and thickness selection and/or monolayer enriched dispersions.

In this paper, we prepared monolayer and multilayer nanosheets of MoS$_2$ and WS$_2$ by LPE. The obtained nanosheet dispersions were size and thickness selected and also monolayer enriched using the LCC method. Optical characterization methods, such as UV-vis spectroscopy and Scanning Electron Microscopy (SEM), were used to assess the size and thickness of the nanosheets. Two-terminal devices were built using a spreading method on electrochemically inert electrodes. The I-V characteristic shows a non-linear transport behavior.

Bulk powders of MoS$_2$ and WS$_2$ were purchased from Merck with purity $>99\%$ and particle sizes $<2 \mu m$. Sodium cholate hydrate (SCH) was purchased from Merck at 99% purity and used as received.

The powders were dispersed in deionized water, exfoliated by sonication, and selected by cascade centrifugation. The dispersion of TMDCs was performed by using an ultrasonic unit “Elmasonic S” from Elma Schmidbauer GmbH, while for centrifugation, we used a laboratory centrifuge, “EBA 20” from Hettich.

The surface morphology of samples was analyzed using a scanning electron microscope Evo 50 XVP (Carl Zeiss NTS), provided with the LaB6 cathode.

A Woollam V-VASE (spectroscopic ellipsometer) equipped with a HS-190 monochromator was employed to measure the light absorption. The conventional spectroscopy (light transmission measurements) was done using Starna rectangular fused quartz cuvettes with a path length of 10 mm. The baseline was performed through the cuvette filled only with SCH aqueous solution. Each scan was acquired in the 200–800 nm spectral range with a step of 0.5 nm.

Lateral devices were fabricated on glass substrates using photolithography and lift-off process. The distance between the contacts was 20 $\mu m$. The WS$_2$ and MoS$_2$ layers were deposited by the drop-cast method between Au electrodes, which were deposited by magnetron sputtering. A continuous film of 2D monolayer-rich material is formed between the electrodes during drop casting. Only the nanosheet dispersion with the largest quantity of monolayers is used. The current–voltage characteristics were recorded using a Keithley 4200-SCS system in DC. A compliance current was used in the current–voltage measurements to limit the current through devices.

A liquid phase exfoliation technique adapted from Ref. 22 was used for both MoS$_2$ and WS$_2$. We start with the cleaning of MX$_2$ powders to remove impurities and very small nanosheets as follows: 0.4 g MX$_2$ polycrystalline powder is dispersed by bath sonication for 1.5 h in 20 ml sodium cholate hydrate aqueous solution, with the concentration of 6 g SCH per liter, below its critical micelle concentration. The water from the bath is continuously refreshed to avoid heating above 30 $^\circ$C, and thus, the properties of the sheets are not damaged. SCH decreases the surface tension of water allowing it to penetrate between the MX$_2$ layers to exfoliate them. In addition, SCH molecules are adsorbed by van der Waals interactions to the exfoliated MX$_2$ nanosheet surface by their nonpolar tail, while the headgroup interacts by electrostatic and/or steric repulsions with the liquid and prevents the reaggregation. After dispersion, the obtained solution is divided into two vials that are centrifuged at 5500 rpm for 1.5 h. Thus, the supernatant with impurities is discarded, while the sediment is collected and dispersed in additional 20 ml of SCH solution with a concentration of 2 g SCH per liter. This new dispersion is bath sonicated for 1.3 h.

The resulting solution contains nanosheets with broad size and thickness distributions. In order to efficiently select and separate the various nanosheets by size and to enrich in monolayers the resulting dispersion, the liquid cascade centrifugation (LCC)\textsuperscript{21} method is used.

The LCC method involves that the nanosheet solution to be subjected to a series of centrifugations at increasing rotational speeds. After each centrifugation step (1500 rpm, 2000 rpm, 3000 rpm, 4000 rpm, 5000 rpm, and 6000 rpm), the sediment (which is a collection of nanosheets of a certain mean size and mean thickness) is retained, while the supernatant is subjected to the next centrifugation step for another 2 h leading to an increasing transparency of the supernatant [Fig. 1(a)]. Thus, the heavier, multi-layer nanosheets are removed in each step of the cascade such that the resultant supernatant is highly monolayer enriched. Representative SEM images of the WS$_2$ and MoS$_2$ monolayers, obtained with the LCC procedure after centrifugation at 6 krpm, are shown in Figs. 1(b) and 1(c).

The size-selected sediments are dispersed in aqueous sodium cholate, and each resulting solution is spectroscopically measured to determine the mean size and mean thickness of the nanosheets. Thus, the UV-vis (visible) spectroscopy measurements [Figs. 1(d) and 1(e)] show systematic changes in the extinction spectra due to increasing edge and confinement effects when the mean size and the mean thickness of WS$_2$ and MoS$_2$ nanosheets decrease. The supernatant obtained after centrifugation at 6 krpm is the richest in monolayers.

From these measurements, the average size $\langle L \rangle$ and the average number of layers $\langle N \rangle$ were determined using the following equations:\textsuperscript{22}

\[ \langle L \rangle = \frac{1000 \langle L \rangle_{max} - 7.6}{2.8}, \]

\[ \langle N \rangle = \frac{\langle L \rangle}{1.5}. \]
\[(N) = 2.3 \times 10^{36} e^{-\frac{\lambda_A}{54888}} \quad \text{(for MoS}_2\text{)}, \]
\[(N) = 6.35 \times 10^{-32} e^{\frac{\lambda_A}{8.51}} \quad \text{(for WS}_2\text{)}, \]

where \(I_A\) is the intensity of the A-exciton maximum (denoted by A), \(I_{\text{min}}\) is the intensity of the local minimum (denoted by Min), and \(\lambda_A\) is the wavelength of the A-exciton in nanometers. \(\lambda_A\) is the peak position from the second derivative of the spectrum smoothed by adjacent averaging.

Figures 2(a) and 2(b) show the mean nanosheet length, \(\langle L \rangle\), and mean layer number, \(\langle N \rangle\), plotted as a function of the relative centrifugal force (RCF). The RCF is calculated as \(106.4 f_i^2\), where \(f\) (in krpm) is the centrifugation rate. It is observed that \(\langle L \rangle\) and \(\langle N \rangle\) decrease with the increase in the relative centrifugal force. This finding is valid for both WS\(_2\) and MoS\(_2\).

Size selection and monolayer enrichment are confirmed in Fig. 2(c). \(\langle L \rangle\) is plotted against \(\langle N \rangle\) showing a linear relationship, which demonstrates that larger, thicker nanosheets are well separated from smaller, thinner nanosheets. This relationship holds true for both WS\(_2\) and MoS\(_2\). The final supernatant (obtained after centrifugation at 6 krpm) has a mean nanosheet length of 37.5 nm and 45.1 nm, while the average number of layers is 1.36 and 1.37 for MoS\(_2\) and WS\(_2\), respectively [Fig. 2(c)].

In Fig. 3(a), the structure of the lateral device employed is illustrated. The electrochemically inert Au electrodes are connected through a continuous MX\(_2\) film. Electrical measurements show that typical non-volatile switching curves are obtained for both materials [Figs. 3(b) and 3(c)], when the devices switch between a low resistive state (LRS) and a high resistive state (HRS).

The devices have an ON/OFF current ratio between LRS and HRS of two times for MoS\(_2\) and higher (∼17×) for WS\(_2\) [Figs. 3(b) and 3(c), inset]. Remarkably low programming voltages are also found of 0.55 V and 0.35 V for MoS\(_2\) and WS\(_2\), respectively. These devices are suitable for energy efficient and high-performance applications because the low switching voltage translates into low energy consumption.

Regarding the conduction mechanism in these devices, it is usually assumed that charge-trapping effects are responsible for the resistive switching (RS) observed in memristive devices based on solution processed 2D nanosheets with electrochemically inert electrodes. Large amounts of traps are expected when nanosheets are overlaid.
Lateral devices based on 2D materials are known to have larger energy consumption than vertical devices.\textsuperscript{24,25} However, we found a high energy efficiency in monolayer-rich 2D WS\textsubscript{2} lateral devices (0.35 V), even higher than in multi-layer 2D WS\textsubscript{2} vertical devices (0.6 V).\textsuperscript{23} Thus, we conclude that the enhanced energy efficiency observed in our devices might be due to the rich monolayer content of the active material.

In summary, we prepared monolayer and multilayer nanosheets of MoS\textsubscript{2} and WS\textsubscript{2} by LPE. The nanosheets were monolayer enriched and size selected using the LCC method. UV-vis spectroscopy was used to assess the mean size and mean thickness of the nanosheets from the sediments and the final supernatant. An average thickness of \(\sim\)1.36 layers with a lateral size of 37.5 nm and 45.1 nm for MoS\textsubscript{2} and WS\textsubscript{2}, respectively, was found. The I-V characteristic of...
two-terminal devices shows a nonvolatile resistance switching effect with very small programming voltages of 0.55 V and 0.35 V for MoS$_2$ and WS$_2$, respectively, which demonstrates the high energy efficiency of the devices. The findings from this study show the potential to achieve energy efficient and high performing memristors based on 2D semiconductor materials for brain inspired computing applications.

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