This article can be cited before page numbers have been issued, to do this please use: Q. Zhang, W. Bao, A. Gong, T. Gong, D. Ma, J. Wan, J. Dai, J. Munday, J. He, L. Hu and D. Zhang, Nanoscale, 2016, DOI: 10.1039/C6NR01534D.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
High-Sensitivity, Highly Transparent, Gel-Gated MoS$_2$

Phototransistor on Biodegradable Nanopaper

Qing Zhang$^{1,2}$, Wenzhong Bao$^{2,3}$, Amy Gong$^2$, Tao Gong$^4$, Dakang Ma$^4$, Jiayu Wan$^2$, Jiaqi Dai$^2$, Jeremy N. Munday$^4$, Jr-Hau He$^{*,3}$, Liangbing Hu$^{*,2}$, Daihua Zhang$^{*,1}$

1. State Key Laboratory of Precision Measuring Technology & Instruments, College of Precision Instrument and Opto-electronics Engineering, Tianjin University, Tianjin 300072, China
2. Department of Materials Science and Engineering, University of Maryland College Park, Maryland 20742-4111, USA
3. Computer, Electrical and Mathematical Sciences and Engineering (CEMSE) Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia
4. Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland 20742-4111, USA

Email: dhzhang@tju.edu.cn, binghu@umd.edu, rhau.he@kaust.edu.sa
ABSTRACT:

Transition metal dichalcogenides hold great promise for a variety of novel electrical, optical and mechanical devices and applications. Among them, molybdenum disulphide (MoS$_2$) is gaining increasing attention as the gate dielectric and semiconductive channel for high-performance field effect transistors. Here we report on the first MoS$_2$ phototransistor built on flexible, transparent and biodegradable substrate with electrolyte gate dielectric. We have carried out systematic studies on its electrical and optoelectronic properties. The MoS$_2$ phototransistor exhibited excellent photo responsivity of ~1.5 kA/W, about two times higher compared to typical back-gated devices reported in previous studies. The device is highly transparent at the same time with an average optical transmittance of 82%. Successful fabrication of phototransistors on flexible cellulose nanopaper with excellent performance and transparency suggests that it is feasible to achieve an ecofriendly, biodegradable phototransistor with great photoresponsivity, broad spectral range and durable flexibility.

KEYWORDS: Molybdenum Disulfide phototransistor, Nanopaper substrate, Flexible electronics, Biodegradable electronics, Gel-electrolyte gating

Main text:

Printed electronics with flexibility has attracted tremendous interests in recent years.
Conventional electronics are made with a glass or plastic substrate. Glass substrates can endure very high handling temperature \(^2\) but provide poor flexibility. Plastic substrates are transparent and flexible,\(^5\) but they are not environmentally friendly and may take hundreds of years to decompose. Recently, ultra-smooth transparent nanopaper with optical transmittance over 90\% has been developed for flexible electronics.\(^6-9\) Nanopaper is made from the same natural wood pulp material as in paper, while consisting of much thinner nanofibrillated cellulose (NFC) fibers of 5 to 10 nm in diameter.\(^10-12\) The wood fibers are treated with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)\(^13,14\) to convert the hydroxyl groups to sodium carboxylate groups for improved packing density.\(^15-18\) The fibers are then disintegrated by high pressure mechanical homogenizer.\(^9\) The densely packed nanofibers leave minimal amount of air trapped in the paper and give rise to very high transparency. Their ultra-small diameter also makes the paper surface sufficiently smooth to be used as the supporting substrate for a variety of functional nano-devices. Furthermore, the use of biodegradable natural wood pulp ensures the device is environmentally friendly at the same time.\(^1\) In a typical CMOS chip, the functional section is formed by only a small portion of the chip, whereas the supporting substrate comprises more than 99\% of the semiconductor materials.\(^19\) These ecofriendly transistors can help conserve non-renewable natural resources by replacing toxic semiconductor materials with biodegradable nanopapers.\(^2\)

Phototransistor is essentially a light-sensitive field effect transistor (FET) that transduces incoming photo energy to electrical current. Phototransistors based on two dimensional (2D) materials have become increasingly popular in recent years.\(^20-22\) Among them, MoS\(_2\) has received particular interest due to its unique electrical and optical properties.\(^23-26\) In fact, devices made of bulk MoS\(_2\) have emerged decades before.\(^27-29\) Its special band structure, mechanical flexibility
and ease of processing make MoS$_2$ an ideal candidate material for optoelectronics applications.$^{30}$ Many groups have reported on MoS$_2$-based phototransistors fabricated on Si/SiO$_2$ substrates, which were neither flexible nor environmental friendly.$^{31, 32}$ In this work, we demonstrate a flexible, transparent and biodegradable phototransistor gated through gel-electrolyte. Two sheets of nanopaper are used as the supporting substrate and the top passivation layer to sandwich the MoS$_2$ channel and the gel-electrolyte in between. We used multilayer MoS$_2$ as they possess higher density of states in conduction band and yield higher photo current compared to single layer crystals according to theoretical predictions.$^{34}$ We have systematically characterized the electrical and optoelectronic properties as well as the optical transmittance of the phototransistor. The device exhibits exceptionally high photoresponsivity ($\sim$1.5 kA/W) and excellent optical transmittance ($\sim$82%).
Figure 1. Three-dimensional schematic and cross-sectional view of the MoS$_2$ phototransistor on transparent and flexible nanopaper (The top passivation layer is not included in this illustration).

Figure 1 illustrates the device structure prior to passivation. 50 nm thick gold electrodes were deposited on top of a mechanically exfoliated MoS$_2$ flake through shadow mask. We chose shadow mask over standard photolithography to avoid dissolving the nanopaper with wet processes. The shadow mask also minimizes process-induced contaminations and ensures good contact quality between the MoS$_2$ and metal electrodes. We then coated a thin layer of gel-electrolyte (1 M LiClO$_4$ in w/w = 1:10 polyethylene oxide, see SI file) on top of the MoS$_2$ flake as the gate dielectric. To immobilize the gel-electrolyte and protect the active area, we covered the surface with a separate sheet of nanopaper to form a conformal seal. The entire process flow of the sandwich structure is summarized in Fig. 2A and in SI file.

Figure 2. A. Fabrication process of the phototransistor. B. Photograph of a sealed phototransistor. C. Optical image of zoom-in area of the phototransistor with MoS$_2$. D. An atomic force microscope image of the phototransistor.
The photograph in Fig. 2B shows a sealed device. The blue dashed line identifies the edge of the top sealing nanopaper. The size is large enough to cover the entire MoS$_2$ flake and the electrodes, while small enough to expose the metal pads for probing or wire bonding. The microscope image of Fig. 2C zooms into the active area of the device. The MoS$_2$ flake at the center serves as the photo-sensitive channel. An atomic force microscopy image is shown in Fig. 2D. Thickness of the MoS$_2$ flake was measured to be 25 nm.

**Figure 3.** Room temperature electrical and optoelectrical properties of the MoS$_2$ phototransistor. A. Output ($I_{ds}$ - $V_{ds}$) characteristics of the phototransistor under different gate voltages. B. Room temperature transfer characteristics ($I_{ds}$ - $V_{gs}$) of the same phototransistor at different source-drain biases. C. $I_{ds}$ - $V_{ds}$ at $V_{gs} = 0$V before (black) and after (red) exposure to laser illumination. The power of the incident laser is 15 µW, and the wavelength is 532 nm. D.
Transfer characteristics ($I_{ds} - V_{gs}$) before (black) and after (red) exposure to laser. The inset shows the same data in log scale.

The electron transport properties of the phototransistor are characterized at room temperature in atmosphere. Before the characterization, we took an I-V measurement on a blank nanopaper and estimated the leakage current to be < 2pA under 5V (SI file). Fig. 3A shows the $I_{ds} - V_{ds}$ curves under four different gate biases, which are linear and symmetric, indicating good contact quality between the MoS$_2$ channel and Au electrodes. The lithography-free fabrication eliminates the need of adhesion metals and prevents contaminations associated with wet processes, resulting in highly stable conductance and superior carrier mobility compared to previous work (see SI file).

The transfer curves ($I_{ds} - V_{gs}$) of the MoS$_2$ phototransistor are presented in Fig. 3B, revealing a typical n-type semiconducting behavior, which is consistent with previous reports.\textsuperscript{4, 6, 8, 9} Fig. 3C shows the $I_{ds} - V_{ds}$ curves of the phototransistor when illumination is on (red) and off (black), respectively. Under stable and continuous illumination (532 nm, 15µW), the incident laser can generate a significant photocurrent in the phototransistor. We compare the transfer characteristics with (red curve) and without (black curve) the illumination in Fig. 3D. In the dark state, the phototransistor shows a threshold voltage of $V_t = 0.4$ V, which shifts to $V_t = 0.1$ V when the illumination is on.
Figure 4. Photo response of the MoS$_2$ phototransistor. A. Photoresponsivity of the device as a function of illumination power. The fitting uses $R \sim E^{\beta-1}$, where $E$ is the illumination power; $\beta$ is the constant B. Photocurrent of the same MoS$_2$ device at different wavelengths under $V_{ds} = 1$ V and $V_{gs} = 0$ V. The inset shows the absorption curve of the MoS$_2$.

We further explored the photo detection performance of the device, characterized by its external photoresponsivity $R$, defined as the ratio of the photocurrent ($I_{pc}$) and the incident illumination power ($P_{in}$):

$$R = \frac{I_{pc}}{P_{in}}$$

As shown in Fig. 4A, the responsivity decreases with increasing illumination power (E), which is consistent with the observation in previous studies. A quantitative correlation between $R$ and $E$ can be written as:

$$R \sim E^{\beta-1}$$

The equation has been successfully applied to other phototransistors based on single-layer MoS$_2$. 
By fitting the data (in SI file), we derived to be 0.26. The parameter reflects the recombination dynamics of photo induced carriers \(^{39}\) and ranges between 0.2 to 0.7 in previous studies.\(^ {39, 40}\) The decrease in responsivity with incident optical power is commonly observed in phototransistors according to other reports.\(^ {20, \text{Error! Bookmark not defined.}, 41}\) This effect is presumably associated with a reduction of the number of photo generated carriers available for extraction under high photon flux due to Auger processes or the saturation of recombination and trap states that influence the lifetime of the generated carriers.\(^ {39}\) In addition, we note that the responsivity of our device is considerably higher than the average value reported in literatures. The maximum value reached 1.5 kA/W at 10nW illumination power (see SI file for more information), while the highest responsivity measured with back gated MoS\(_2\) phototransistors are typically below 1kA/W.\(^ {26, 30}\) We believe both the lithography-free fabrication and the electrolyte gating contribute to the responsivity enhancement, and the latter plays a more dominant role. The electrolyte we used is a liquidized salt that contains cations (Li\(^+\)).\(^ {33}\) The cations accumulate on MoS\(_2\) surface under an externally applied voltage, forming an electric double layer (EDL). The EDL is able to effectively screen charge impurities and reduce electron scattering, thereby largely boosting the carrier mobility by 1 to 2 orders of magnitude.\(^ {42}\) At the same time, the electrolyte can also induce strong band bending at the MoS\(_2\)/Au interface and significantly lower the Schottky barrier.\(^ {43, 44}\) The large enhancement in both intrinsic and extrinsic mobility is presumably the reason for the exceedingly high responsivity observed in our phototransistors.

We have also measured the dark/light current across a wide range of wavelengths (Fig. 4B). When the incident laser is above 685 nm, the photocurrent drops sharply with increasing wavelength. The transition around 685 nm corresponds to the excitation of electrons across the bandgap (1.81eV) of multilayer MoS\(_2\). The same transition is also evidenced in the absorption
curve in the inset. Below 685 nm, the slow and monotonic increase in photocurrent with
decreasing wavelength (or increasing photon energy) is presumably due to the fact that higher
energy photons can excite electrons to higher energy states, resulting in a larger number of
photocarriers that can overcome local energy barriers in the conduction channel and/or at the
MoS$_2$/metal interface.

**Figure 5.** Optical transmittance, transparency and flexibility of the MoS$_2$ phototransistor.
A. Optical transmittance of a single sheet of nanopaper (black line) and a MoS$_2$ phototransistor
sandwiched between two layers of nanopaper (red line). B. Photograph of an array of
phototransistors showing high transparency. C. Transfer characteristics of the phototransistor without illumination (blue), under illumination but without passivation (red), and with both illumination and passivation (black). D. The device can be largely bended, exhibiting great flexibility.

Besides excellent photoresponsivity, the phototransistor is highly transparent and flexible at the same time. In Fig. 5A, we compare the optical transmittance of the device (red curve) with a sheet of bare nanopaper (black curve) across a broad spectral range from 400 nm to 1100 nm. When compared at 550 nm, the optical transmittance of the phototransistor (82%) is slightly lower than that of the bare nanopaper (85%) due to the addition of gel-electrolyte and passivation layer. Fig. 5B and 5D demonstrate the excellent flexibility of the device and its compatibility with large-scale integration. The electrical and photodetection properties remain nearly the same before and after bending (in SI file). To verify that the passivation layer induces negligible perturbation to the phototransistor, we have recorded the transfer curves before and after passivation (Fig. 5C). In the dark state, the two devices behave the same as indicated by the data points in blue triangle. Under illumination (532 nm), the bare device shows slightly higher current compared at the same gate bias. The difference at $V_{gs} = 3$ V is approximately 6 $\mu$A between the two devices. The result is in good agreement with the optical transmittance response in Fig. 5A, in which the sealed phototransistor has a slightly lower optical transmittance therefore less sensitive to the incident laser.

Summary

We have demonstrated an electrolyte gated phototransistor based on multilayer MoS$_2$. The device uses highly transparent, flexible and biodegradable nanopaper as both the supporting substrate
and passivation layer. It exhibits excellent photoreponsivity of approximately 1.5 kA/W under 10nW illumination power, considerably higher than typical back gated phototransistors reported in other studies. The device functions across a broad spectral range with excellent stability under sustained voltage bias and illumination. These properties make the device highly attractive for various industrial applications including touch sensor panels, image sensors, solar cells, and intelligent displays.

EXPERIMENTAL SECTION

**Fabrication of Transparent Nanopaper.** The nanopaper was fabricated by previously established method published by Zhu. et al. The experimental procedure includes three major steps: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) oxidation reaction, Büchner filtration, and disintegration through a microfluidizer (M110 EH, Microfluidics Inc., USA). TEMPO-mediated oxidation started by adding and dissolving 78 mg TEMPO into 25 mL buffer solution. The buffer consists of 0.08 M Sodium carbonate (Na$_2$CO$_3$), and 0.02 M Sodium bicarbonate (NaHCO$_3$). Combine three solutions, that is, 78 mg TEMPO in 25 mL buffer, 514 mg of sodium bromide (NaBr) in 50 mL buffer and 5 g dry weight of Kraft bleached softwood pulp in 115 mL buffer solution. The solution was stirred at a speed of 700 rpm with IKA RW20 digital mixer for 10 min followed by drop-wise addition of 35 mL sodium hypochlorite (NaClO). The pH value of the solution was measured every 20 mins and kept at pH=10.5 by adding 3M sodium hydroxide (NaOH) for 2 hours. Reaction with continuous stirring 700 rpm lasted overnight at room temperature. Then, the TEMPO-oxidized fibers were transferred to a vacuumed flask and funnel for Büchner filtration using 0.65 μm nitrocellulose ester filter (Millipore DAWP29325) to
wash away the reagents. Fiber was washed by 1L deionized (DI) water by stirring at 800 rpm for 30 min and passing through Büchner funnel into a flask twice. The resulting fiber cake was dissolved in DI water to form a 1 wt% solution and passed through a microfluidizer with thin z-shaped chambers. The channel dimension was 200 µm and the process pressure was 25,000 psi. After passing through the microfluidizer the fibers were dispersed in water to create a 1 wt% nanofibrillated cellulose (NFC) solution. The NFC solution was further diluted with DI water to 0.2 wt% and mixed at 500 rpm for 10 min with IKA RW20 digital mixer. After that, the dispersion was degassed in a bath sonicator for 20 min, and passed through a 0.65 µm pore size nitrocellulose eater filter (Millipore DAWP29325). The cake formed was compressed between a PET film (on top) and papers supported by iron plate (below). Then, it was transferred to a hot pressing machine in 105 °C for 4-5 days to form nanopaper with a fiber diameter of about 5 nm.

Reference:


