

Graphene on Paper: A Simple, Low-Cost Chemical Sensing Platform

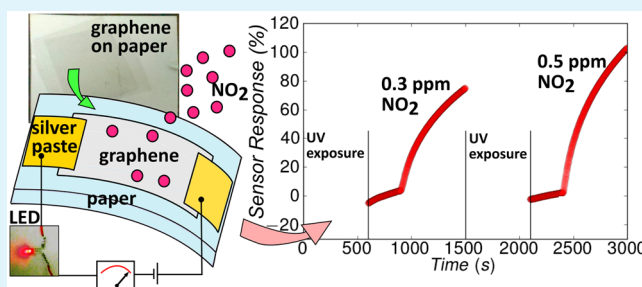
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S Supporting Information

ABSTRACT: Graphene layers have been transferred directly on to paper without any intermediate layers to yield G-paper. Resistive gas sensors have been fabricated using strips of G-paper. These sensors achieved a remarkable lower limit of detection of ~ 300 parts per trillion (ppt) for NO_2 , which is comparable to or better than those from other paper-based sensors. Ultraviolet exposure was found to dramatically reduce the recovery time and improve response times. G-paper sensors are also found to be robust against minor strain, which was also found to increase sensitivity. G-paper is expected to enable a simple and inexpensive low-cost flexible graphene platform.

KEYWORDS: graphene, paper, gas sensors, graphene transfer, graphitic sensors



Low-cost chemical sensing platforms can bring benefits of medical diagnostics and environmental and food monitoring to a large section of humanity. Sensing platforms utilizing material properties are better suited for low-cost applications than optical or spectroscopic techniques. The former trade off the wide range and specificity of the latter for lower cost, easy fabrication, portability, and robustness to ambient conditions. Such platforms include metal-oxides,¹ conjugated polymers,² nanowires,³ carbon nanotubes (CNTs),⁴ and most recently, graphene. Of these, graphene stands out as a material for chemical sensing. It is only a single atom thick, which makes it extremely sensitive to changes in its chemical environment.^{5,6} It can be modified or functionalized in a number of ways to make the response selective to a desired chemical. This combination of high sensitivity with desired selectivity is not seen in the other materials listed above, except perhaps, CNTs. Although the performance of graphene sensors is expected to be comparable to those based on CNTs, control of processing and hence properties over large areas is easier with graphene than with CNTs.

A challenge in using graphene for widespread chemical sensing is to lower the cost of fabricated devices. Currently graphene is deposited by chemical vapor deposition (CVD) on Cu and then transferred to various substrates such as SiO_2/Si for further device processing. Developments such as roll-to-roll processing on reusable Cu foil substrates are expected to bring down the cost of the starting graphene itself.^{7–9} However, on the device fabrication side, expensive techniques like lithography on Si-based substrates are still used to fabricate graphene devices and sensors. Reducing device cost calls for cheaper substrates and simpler fabrication methods.

To enable low-cost devices, we have transferred CVD graphene directly on to paper to yield what we will call “G-paper”. To the best of our knowledge, this is the first report of

direct graphene transfer onto paper without any intermediate layers. Paper is one of the cheapest and most abundant materials known to mankind. Recently, there has been a surge in efforts to put it to good use as a functional and structural material for flexible microscale devices. Paper-based electronics,¹⁰ microfluidics,¹¹ and simple devices¹² have already been demonstrated. Following transfer of graphene to paper, sensing strips are formed by simply painting contacts at the ends of G-paper. Such G-paper sensors show a lower limit of detection of ~ 300 ppt of NO_2 . This sensitivity exceeds or is close to that of other graphitic sensors using paper as substrate^{13–16} and semiconducting metal oxide (SMO) sensors.¹⁷ Although graphene-based sensors have shown better sensitivities, the simplicity and low-cost of fabrication make G-paper sensors better suited for widespread use. The easily tunable selectivity of graphitic carbons^{13,15,16} will make G-paper a versatile platform for sensing, whereas the smaller resistance of the G-paper strips will lower demands on energy and instrumentation. The flexibility of G-paper and its effect on the sensing characteristics has also been studied here.

CVD graphene has been transferred onto various flexible substrates,¹⁸ but transfer of graphene on bare paper has not yet been reported. Using a method described in the Supporting Information, graphene was transferred on to routine printing paper and a smooth glossy paper (Figure 1a, panels 1–5). As shown in Figure 1a (panel 4), the transfer on normal printing paper is patchy, whereas in comparison, on smooth paper (Figure 1a, panel 5), the transfer is complete. The presence of graphene and its quality was verified by Raman spectroscopy (see the Supporting Information, section 2). The sheet

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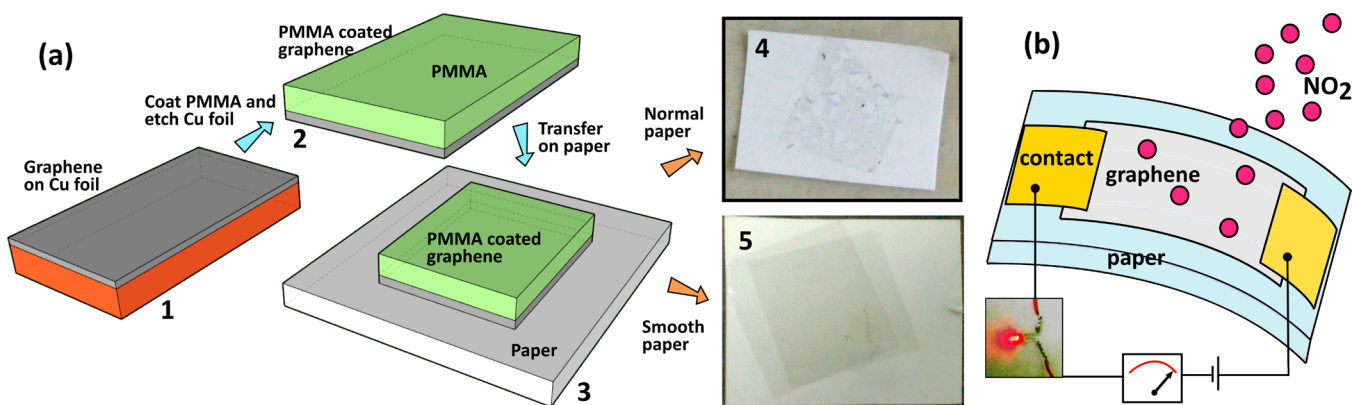


Figure 1. (a) Schematic of graphene transfer process on to paper. Starting with graphene on Cu foil (1), a layer of poly(methyl methacrylate) (PMMA) is spin-coated and Cu is etched to get graphene supported by PMMA (2) in water. PMMA-graphene film is then dredged on to paper (3) and PMMA is dissolved with acetone. Normal paper yields patchy coverage (4) compared to transfer on smooth paper (5). Panel 5 shows two layers of graphene transferred on smooth paper. (b) Schematic of a G-paper strip in action as a gas sensor. The circuit can carry sufficient current to make an LED glow (seen on bottom left corner).

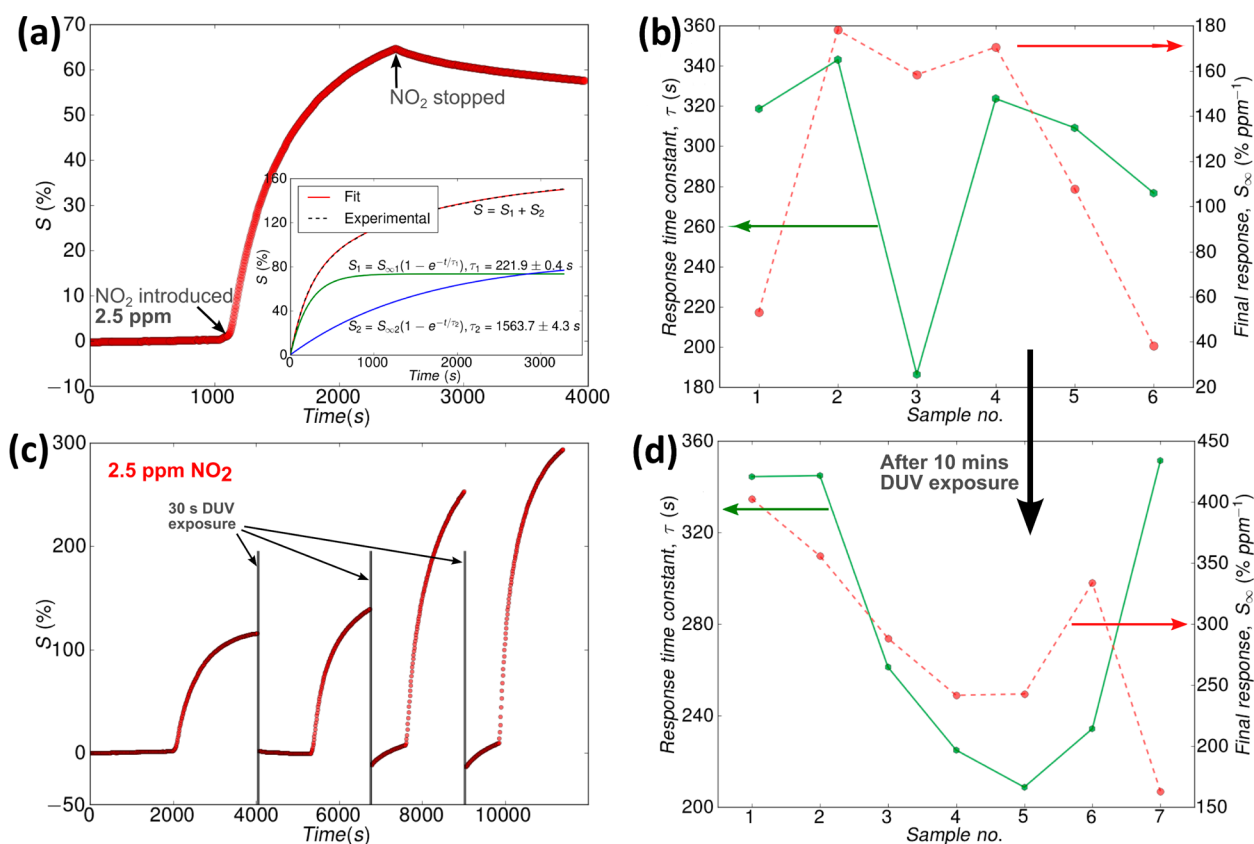


Figure 2. (a) Response of a G-paper strip to 2.5 ppm of NO₂. Inset shows a fit of double exponential function to the temporal response for 2.5 ppm of NO₂. The two constituent exponentials are also shown along with the estimates of time-constants. (b) Final response S_{∞} (normalized for 1 ppm) and response time constant τ for various samples, with average values of 118% ppm⁻¹ and 293 s, respectively. (c) Effect of several 30 s exposures of deep ultraviolet (~ 254 nm, DUV) radiation on a sample. The instant of exposures is indicated by arrows. (d) S_{∞} and τ values for several samples exposed to 10 min of DUV, with averages values of 290% ppm⁻¹ and 281 s, respectively.

resistance, another measure of quality of graphene, was 2.8 ± 0.8 k Ω/\square for G-paper strips (see Table T1 in the Supporting Information). This is comparable to that obtained from SiO₂ substrates (1.2 k Ω/\square), indicating good quality of transfer. The small resistance of the strips is advantageous in applications, because it allows larger sensing current to be achieved. A larger sensing current can be detected by cheaper electronics and can be traded for power consumed by the sensor. A G-paper sample

with width and length of few millimeters, could also sustain a light-emitting diode, which needs currents in the range of mA (Figure 1b).

A large-area, damage-free transfer of graphene requires the receiving substrates to have a smooth and chemically appropriate surface.¹⁸ Optical profilometry showed that the root-mean-square (rms) roughness of normal paper was 7.7 μm (see the Supporting Information, Figure S3), whereas atomic

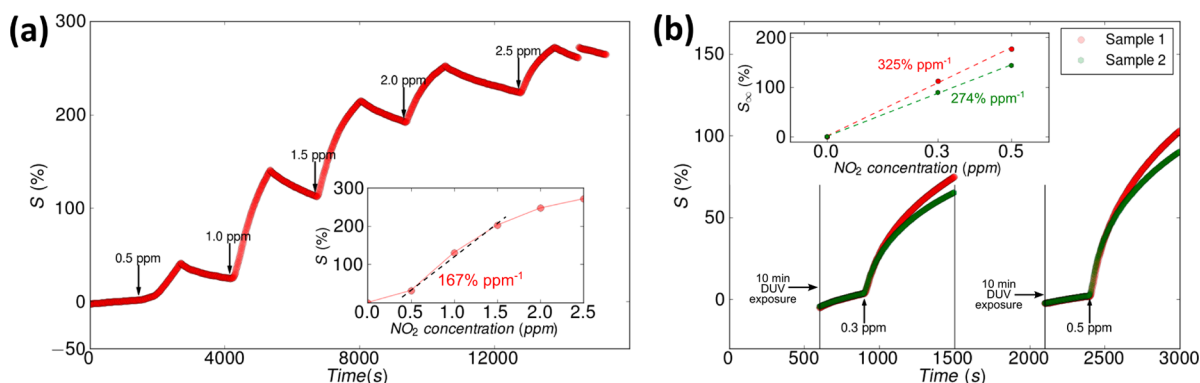


Figure 3. (a) Change in conductance of a sample as concentration of NO_2 increases. The inset shows the plot of response at $t = 1000$ s vs the concentration of NO_2 , which has a slope of 167 ppm^{-1} at the start (indicated by dashed line). (b) Response of two samples that were exposed to 10 min of DUV before being characterized under 0.3 and 0.5 ppm of NO_2 flow. The inset plots the final response S_∞ of the samples vs the concentration of gas. The slopes are also shown.

force microscopy scans yielded the rms roughness of smooth paper to be 55.1 nm (see the Supporting Information, Figure S4). Fillers materials like clays and minerals are generally used to smooth paper.¹⁹ On a rough surface, as in the case of regular printing paper, graphene is supported only on a very small area at the asperities. As a result, there is stress concentration at the contact points. The transfer of graphene involves exposure to and withdrawal of solvents for removal of the polymer support. It is during these events that stresses and stiction forces cause tears. The smaller contact area between graphene and rougher substrates also results in weak adhesion, leading to removal of flakes generated by tearing. These events, tearing and flake removal, are inhibited on the smooth paper.

We characterized the gas sensing performance of G-paper strips using NO_2 as the analyte (see the Supporting Information, Section 1). Figure 2a shows the relative change in conductance of G-paper strips when NO_2 was flown on it. The response S is defined as the relative change in conductance, G , and is given by $S = \Delta G/G = (I - I_0)/I_0 \times 100\%$. I_0 and I are the electrical currents under synthetic air flow and under test gas flow. The strip shows a marked increase in conductance in few minutes of flow of NO_2 ($\sim 65\%$ increase in 1400 s). CVD graphene, which has undergone the transfer process, under ambient conditions is normally p-doped.²⁰ NO_2 , which is a strong electron withdrawing species, increases the p-doping of graphene, when it is adsorbed on its surface. Because of the band structure of graphene, a higher p-doping of already p-doped graphene changes the Fermi level toward higher density of states of carriers, which translates in higher conductance of the strip. On stopping the flow of NO_2 , the conductance starts to drop, but at a much slower rate ($\sim 15\%$ decrease in 1500 s). Five samples were tested for under NO_2 flow and the response for NO_2 was consistent from sample to sample.

The sensitivity and the quickness of response are two crucial parameters for gas sensors. These can be quantified by the Langmuir adsorption model,²¹ giving $S(t) = S_\infty(1 - e^{-(t/\tau)})$, where $S(t)$ is the response at time t , S_∞ is the final response produced by equilibrium coverage at the given pressure, and τ is the characteristic time constant. We find that the conductance vs time data for all the samples in the response stage fit a double exponential model well²² (Figure 2a, inset), $S(t) = S_{\infty 1}(1 - e^{-(t/\tau_1)}) + S_{\infty 2}(1 - e^{-(t/\tau_2)})$. The presence of two time constants indicates that two independent adsorption processes involving the test gases are active on the surface of graphene. We define the quantities $S_\infty = S_{\infty 1} + S_{\infty 2}$ and $\tau =$

$(S_{\infty 1}/(S_{\infty 1}/\tau_1 + S_{\infty 2}/\tau_2))$ to compare the sensitivity and response times for different samples, respectively. The latter is the inverse of the slope of the response-time plot at $t = 0$ normalized by final response (S_∞) of the sample. Response-time curves of several samples under NO_2 flow (2.5 ppm) were analyzed to determine $S_{\infty 1}$, $S_{\infty 2}$, τ_1 and τ_2 (see the Supporting Information, Section 5), which provided S_∞ and τ for each of the samples. These values have been plotted in Figure 2b for the 6 samples tested. A large S_∞ and small τ is desirable for good sensors. Typical values of τ was in hundreds of seconds, somewhat slower than metal-oxide gas sensors,^{17,23} which are currently the fastest responding sensors. The overall response (S_∞) was around $118\% \text{ ppm}^{-1}$ of NO_2 (Figure 2b), which compares well to best sensor materials, including metal-oxides¹⁷ and graphitic carbons (see below).

The slow recovery is caused by relatively stronger binding of test gas molecules to graphene surface. This strong binding also results in smaller response time and higher sensitivity to the gas. Therefore, it is conflicting to reduce response and recovery times of sensor by a single approach. Cleaning and functionalization of graphene are two simple methods to achieve these ends. The latter can selectively make binding of desired gases to graphene surface stronger, improving the response time and sensitivity for them. The former reduces doping of graphene and moves its Fermi energy toward the charge neutrality point, where even a small change in doping of surface can result in large change in electrical properties of graphene. Schedin et al.⁵ have used pristine graphene to detect single gas molecules on graphene surface (under specialized conditions). Cleaning methods can also be used to get rid of adsorbed test gas molecules, thereby improving recovery times. Of the several cleaning techniques available in literature,^{24–27} ultraviolet (UV) light^{28,29} exposure is most appropriate for G-paper. Chen et al.²⁹ have shown ultrasensitive (158 parts per quadrillion of NO_2), reproducible sensing with graphene under constant UV illumination.

We studied the effect of DUV exposures on G-paper samples. A strip was tested under 2.5 ppm of NO_2 flow and then moved into an enclosure housing a DUV lamp. After exposing the sample to DUV radiation for the 30 s, the sample was returned back to the gas test chamber and characterized again. The process was repeated three times and the response curves are shown in Figure 2c. Clearly, DUV exposure was very effective in returning the sample to its original state, recovery time was effectively reduced to 30 s compared to hours noted above. The

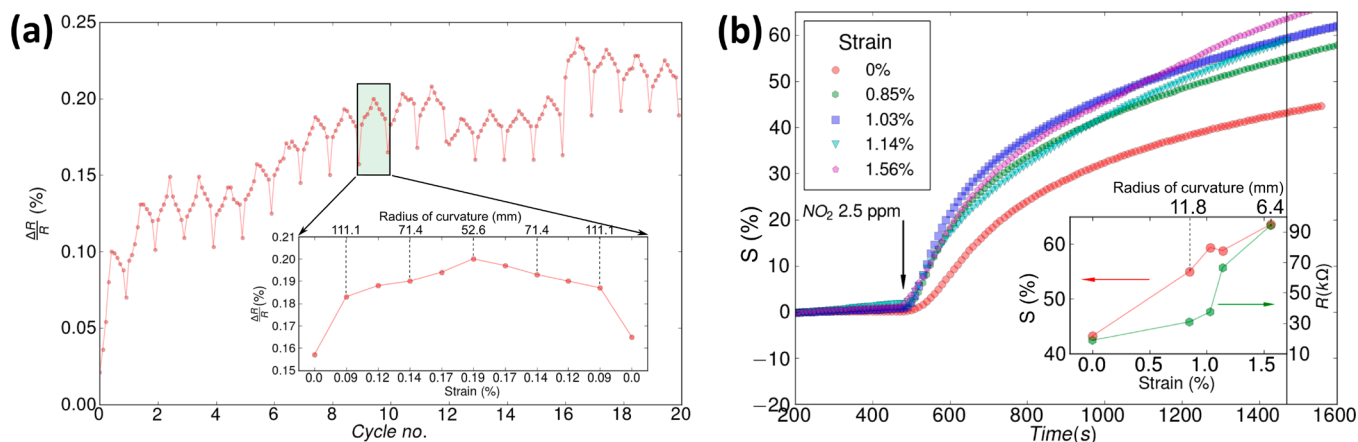


Figure 4. (a) Change in resistance of a g-paper strip on cyclic application of strains. The strains corresponding to a cycle are shown in detailed inset. Same strain values were used in all cycles. (b) The change in conductance of a sample as strain is applied on it under 2.5 ppm flow of NO_2 . The responses were taken for the vertical gray line shown. Inset shows that both the baseline resistance and response of the strip increase with increasing strain.

recovery times are even better than the metal-oxides sensors, which use power consuming high temperatures to reset.¹⁷ We also observe lower values of resting conductance and higher final response with each 30 s DUV exposure, which hints at cleaning of graphene surface. A longer duration exposure (5 min) achieves similar results as three 30 s exposures combined together.

To compare the effect of DUV exposure on S_∞ and τ , we characterized several samples after 10 min of DUV exposure for S_∞ and τ . A lower concentration of 0.5 ppm of NO_2 was used to not to saturate the response. The cleaning of graphene surface resulted in average S_∞ increasing by a factor of 2.5 compared to the nonexposed samples in Figure 2b. The average response time constant τ also improved marginally.

Raman spectroscopy was used to ascertain the changes on the surface of graphene following DUV exposure. Our data (see the Supporting Information, section 6) indicate slight reduction in p-doping levels of the samples, which in turn points to reduction of adsorbents on the surface of graphene.

The response of G-paper sensors at different concentrations of NO_2 is shown in Figure 3a. The sample was exposed to 30 s DUV at the start. The test gas was introduced in the chamber at regular intervals with increasing concentrations and flown for ~ 1000 s. Synthetic air flow was maintained when NO_2 was not flowing. The response of the sample at 1000 s after the start of the flow of NO_2 was used to generate the plot in the inset for Figure 3a. The sample shows increasing response with increasing test gas concentration. The curve can be used to estimate the lower limit of detection (LLD), by comparing the noise level to the slope ($167\% \text{ ppm}^{-1}$, see the Supporting Information, section 1, for error estimates) of the response at the lowest concentration of NO_2 . Assuming the response time (τ) to be similar at all the concentrations used, the slope obtained from the final responses (S_∞) will be same as the slope we have obtained from response at 1000 s. The current noise estimated from the data points at the start (<1000 s) was 0.042% of total current. This yields an LLD of ~ 754 ppt, assuming a signal-to-noise ratio of 3 at LLD according to IUPAC recommendations³⁰ (see the Supporting Information, section 7, for calculations). To see if the LLD can be improved further, we exposed two samples to DUV for 10 min and their response recorded at 0.3 and 0.5 ppm of NO_2 (Figure 3b). The

slopes of final responses S_∞ , plotted in inset of Figure 3b are $325\% \text{ ppm}^{-1}$ and $274\% \text{ ppm}^{-1}$ respectively, from which we obtain an LLD of 387 and 454 ppt, respectively. This performance of G-paper is comparable or better than similar graphitic carbon based sensors made using paper as a substrate. Mirica et al.¹³ reported a sensitivity of $0.25\% \text{ ppm}^{-1}$ for NO_2 , with CNTs and pencil traces on paper. Ammu et al.¹⁵ observed the LLD to be 64 ppt for NO_2 with CNT chemiresistors printed on paper. Using their algorithm for calculations lowers our LLD to 258 and 305 ppt, respectively, for NO_2 (see the Supporting Information, section 7). Estimated error in all these LLD values is 26% (see the Supporting Information, section 1). The LLD shown by G-paper is close to CNT-based chemiresistor sensors, which also display similar response time constants.⁴

The flexibility of paper has contributed to its widespread use, and it is an additional advantage of G-paper sensors as well. It is thus important to get a measure of how the G-papers fare under strain. Large strain can generate cracks in G-paper, which can have large effect on its electrical and sensing properties. We measured the relative change in two-point resistance of a sample of G-paper (Figure 4a) as it was cyclically strained by flexing (see the Supporting Information, Figure S1). The smallest radius to which the samples were bent to was ~ 52 mm (Figure 4a, inset). There is a small drift in the resting value of resistance as the cycles progress, although this drift becomes smaller in later cycles. The response within a cycle was fairly repeatable. The strain–resistance response was replicable over different samples.

The introduction of cracks in graphene layer can be useful for chemical sensing. As shown in Figure 4b when G-paper was subjected to different values of strain, S_∞ increased by a factor of 2 over the unstrained sample. The sample was put under a specified strain and NO_2 was flown on it for some time to record its response. The sample was then removed from the test chamber and exposed to DUV (30 s) to reset it to its original condition and the process was repeated again with different strain value. For large strains applied here (radius of curvature ~ 12 mm or lower), the resistance of the sample changes irreversibly to higher values (Figure 4a, inset). Large strains can produce cracks and other defects in graphene layer, so this behavior is expected. Cracks and defects provide more

sites for adsorption of test gas, as well as bear large effect on resistance when they are bridged. As a result, the response improves as depicted in the inset of Figure 4b. Our data (see the Supporting Information, section 8) shows that the increase in response is almost entirely caused by increase in the response associated with long time constant ($S_{\infty 2}$), there is almost no change in $S_{\infty 1}$. This indicates that the longer time response is related to defects or cracks in graphene.

In conclusion, we have demonstrated a simple process for making graphene on paper-resistive sensors. The room-temperature NO_2 sensing performance of these sensors is close to or better than the state-of-art graphitic sensors made with paper as substrate or metal oxides sensors operating at elevated temperatures. With DUV exposure, the speed of response remains only slightly higher than fastest metal-oxide sensors. Recovery times, on the other hand, drastically reduce to tens of seconds, which are among the fastest. The combination of advantages provided by G-paper makes them a suitable platform for low-cost, environmental friendly, and widely deployed sensing.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details. Raman spectra for G-paper. Roughness comparison of normal and smooth paper. Sheet resistance of G-paper. Detailed for calculation of S_{∞} and τ . Characterization of DUV treatment on G-paper using Raman spectroscopy. Algorithm for determination of current noise levels. Correlation of response to strain induced changes in resistance of G-paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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