Supporting Information

Paper-Supported Graphene-Ionic Liquids Array for E-nose Application

*Xiangrong Zhu[a], Dong Liu[a], Qiaofen Chen [a] Leimiao Lin[a], Shuling Jiang[a], Hongzhi Zhou[a], ,Jiayin Zhao[b],Jianmin Wu**

[a]*Institute of Microanalytical System, Department of Chemistry, Zhejiang University, Hangzhou, 310058, China*

[b]*Wuxi entry exit inspection and Quarantine Bureau, WuXi,214101,China*

Corresponding author: Jianmin Wu

Email address: wjm-st1@zju.edu.cn

EXPERIMENTAL SECTION

Reagents The ILs used in this work were1-butyl-3-methylimidazolium trifluoromethanesulfonate (BmimOTf), 1-butyl-3-methylimidazolium perchlorate ($BmimClO_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$), 1-Butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) and hexyltriethylammonium bis(trifluoromethanesulfonyl)imide ($N_{6,2,2,2}NTf_2$). All ILs were purchased from Lanzhou institute of Chemical Physics, Chinese Academy of Science (CAS). Graphene oxide (GO) sol was purchased from Chengdu institute of Organic Chemistry, Chinese Academy of Science (CAS). The characterization of GO sample was conducted by CAS (Http://www.timesnano.com). Hydrazine hydrate and acetonitrile were purchased from Aladdin Co. (China). All reagents were of analytical grade and used as received. The filter paper was purchased from Sinopharm Chemical Reagent Co. (China). The standard gas samples including NO_2 (20 ppm), Cl_2 (20 ppm), toluene (200 ppm) and hexane (200 ppm) were purchased from Hangzhou Xinshiji Gas Co. (china), the pure air and N_2 were purchased from Hangzhou Jingong Gas Co. (China).

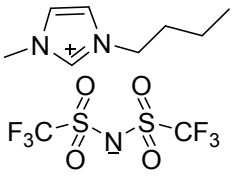
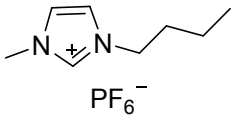
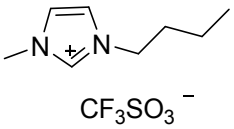
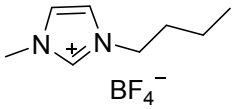
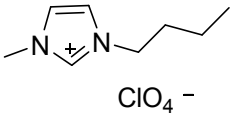
Material Characterization The morphology of filter paper after GO loading was observed with a field emission scanning electron microscope (Utral 55, CorlzeisD, Germany). Raman spectroscopy of paper supported graphene samples were characterized with a Raman spectrosmeter (LabRamHRUV, JDbin-yvon, France). The surface chemistry of graphene loaded paper were characterized with X-ray photoelectron spectrometer (Escalab 250Xi, ThermoFisher, England).

Measurement of current response Concentration of gas sample was adjusted by a gas mixing apparatus (National Institute of Metrology, China). The total flow rate of the mixture was kept at 200 $ml \cdot min^{-1}$. The sample was then admitted to a PMAA chamber clamped with the paper-supported rGO-IL sensing array. The voltage applied on each chemirisistive sensing element was set at 3.0 V, and the electrical current flow through each sensing element was measured with a homemade multichannel amperometer. Real-time current change was recorded with a Labview software.

Data processing algorithm and data analysis The electrical signal on each sensing element in response to gas sample was normalized using the equation: $R=(I-I_0)/I_0$, where R is the normalized conductance response after exposing the senor to gas analyte. I_0 is the baseline of electrical current measured in pure nitrogen stream, and I is the current measured after exposing the sensor to analytes. Principal component analysis (PCA) was performed using SPSS software to plot the response pattern of the sensor array.

Supplementary Table

Table S1 The list of ionic liquids.

Ionic liquids	Structure	Ionic liquids	Structure
$BmimNTf_2$ **(1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide)**		$BmimPF_6$ **(1-butyl-3-methylimidazolium hexafluorophosphate)**	
BmimOTf **(1-butyl-3-methylimidazolium trifluoromethanesulfonate)**		$BmimBF_4$ **(1-Butyl-3-methylimidazolium tetrafluoroborate)**	
$BmimClO_4$ **(1-butyl-3-methylimidazolium perchlorate)**			

Supplementary Figures

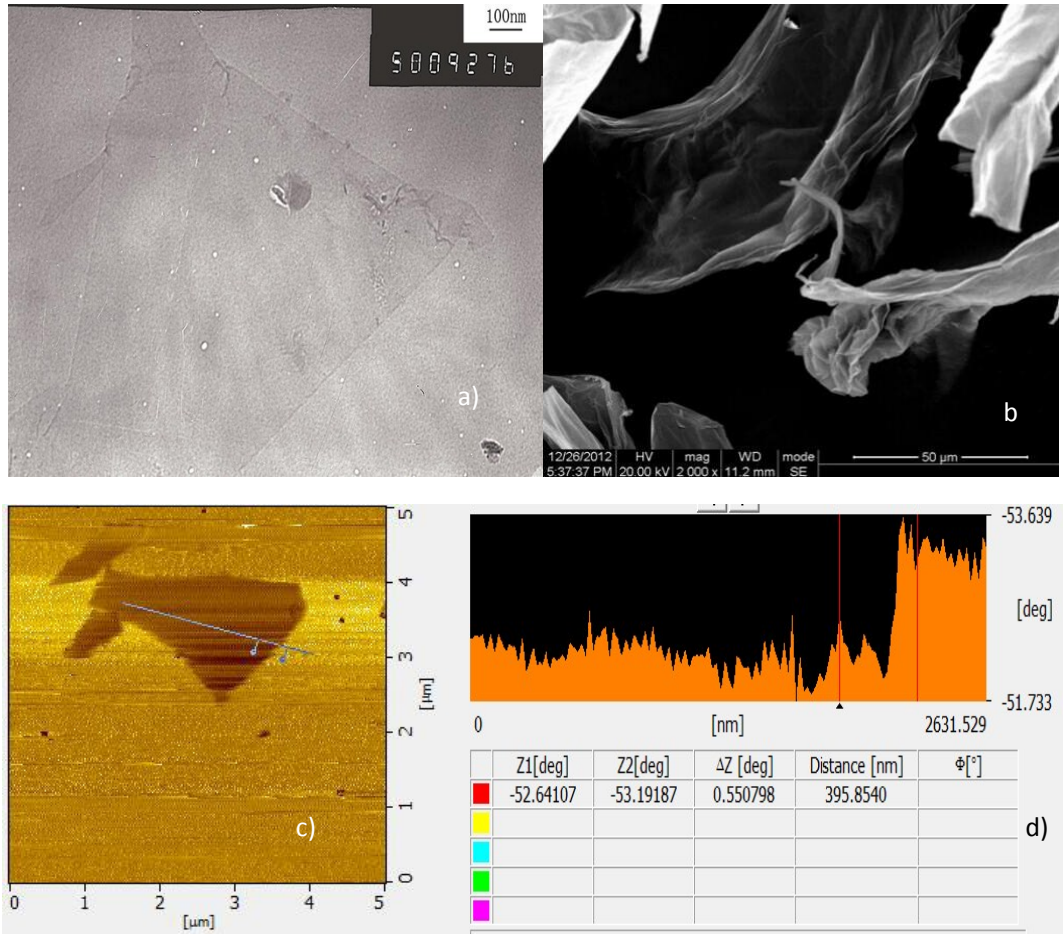


Figure S1. Characterization of GO sample. (a) TEM , (b) SEM, (c, d) AFM indicated that thickness of the GO sample is 0.55~1.2 nm, the size is 0.5~3 um, the GO sheet layers are estimated to be less than 3.

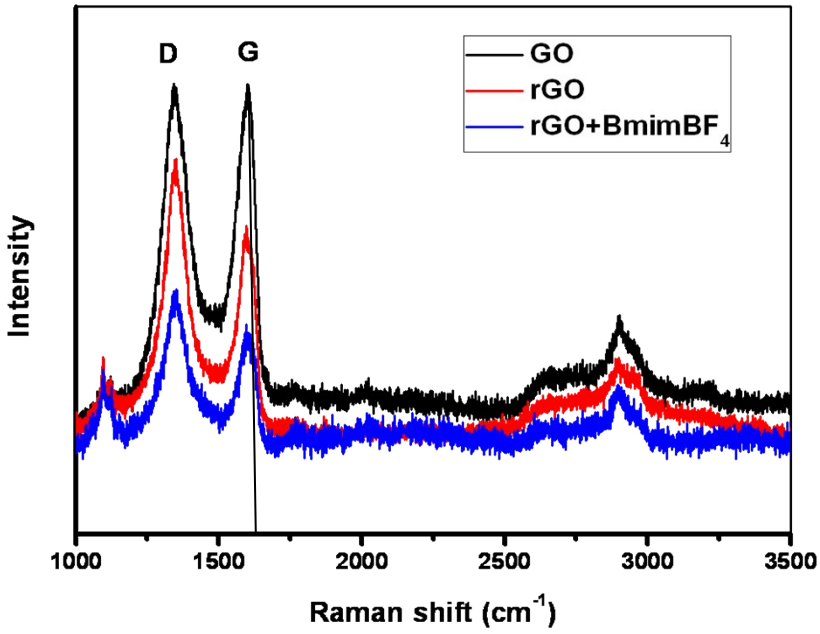


Figure S2. In-situ Raman spectra of GO, rGO and rGO/$BmimBF_4$ sample supported on filter paper. GO exhibit G-mode and D-mode peaks, which arise from the vibration of sp^2-hybridized carbon atoms in a 2D hexagonal lattice with dangling bonds in disordered plane terminations, respectively. The rGO and rGO/$BmimBF_4$ also display two characteristic peaks of D and G, whose intensity ratio (I_D/I_G) increased due to the reduction of GO.

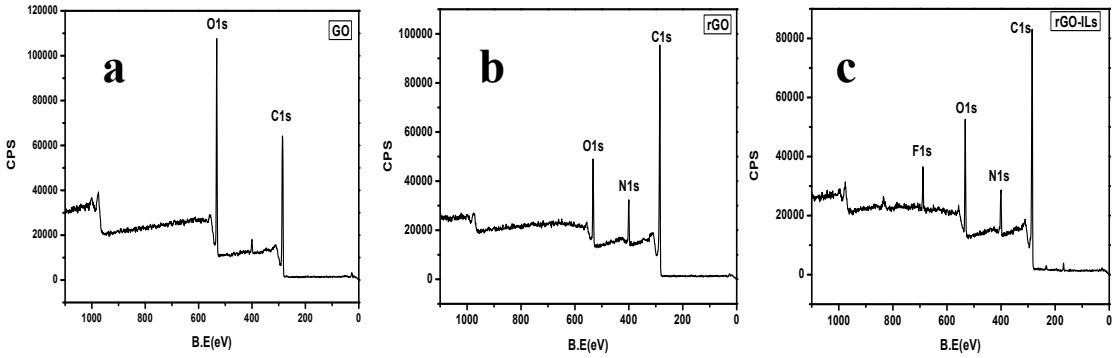


Figure S3. The XPS spectra of (a) GO, (b) rGO and (c) rGO-$BmimBF_4$ sample supported on filter paper. The oxygen peak (O1s, 532.67 eV) found on the rGO sample decreased significantly, which is an indicative of partial reduction of the rGO sample. Compared with GO sample, the peak of elemental carbon slightly increased after reduction, owing to the increase of relative content of carbon atom on rGO surface. After the rGO was modified with $BmimBF_4$, the peak of elemental fluoride (F1s, 688.78 eV) was observed, confirming the adsorption of $BmimBF_4$ on the rGO surface.

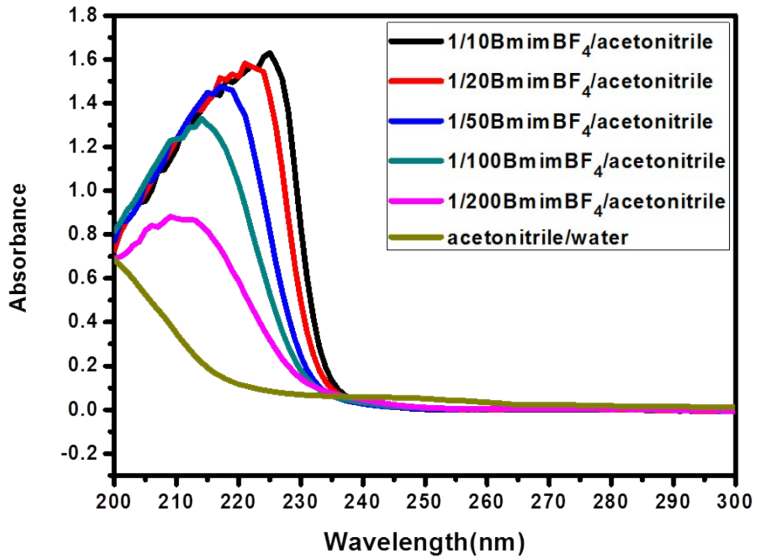


Figure S4. The Ultraviolet absorption spectra of acetonitrile solution eluted from the paper supported rGO adsorbed with different concentrations of $BmimBF_4$. Each sample adsorbed with IL was immersed in acetonitrile solvent for 2 hours. The UV spectra of eluent displayed a same absorbance peak as that of $BmimBF_4$ solution, thereby confirming the adsorption of the IL on rGO surface. With the increasing of $BmimBF_4$ content adsorbed on rGO surface, the larger UV sbsorption was found in the corresponding eluent. The results indicated that the content of ionic liquids adsorbed on rGO surface can be effectively adjusted by the passing through IL/MeCN solution with different volume ratio.

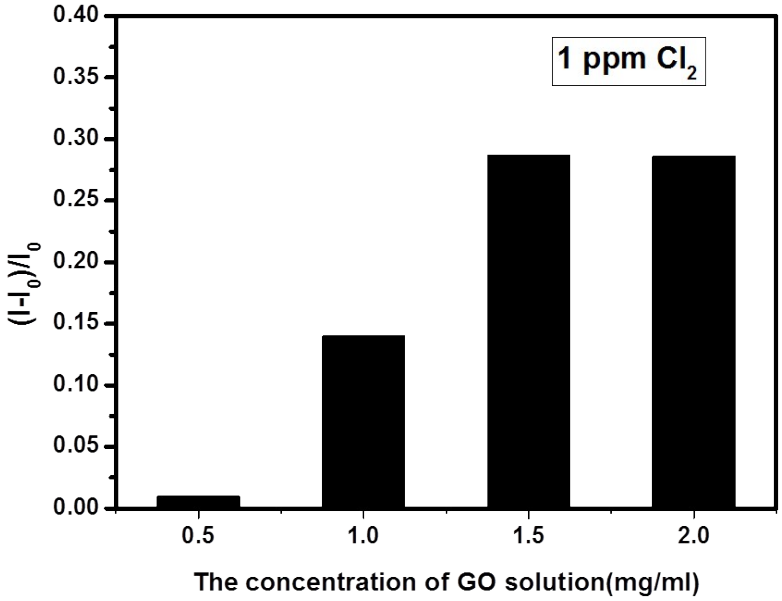


Figure S5. The effect of GO concentration on the conductance response generated by the paper supported rGO-$BmimBF_4$ sensor towards 1 ppm of Cl_2. Paper chips loaded with different amount of rGO were prepared by filtrating through GO solution with different concentration. After hydrazine reduction, the resistance response of each rGO paper chip towards 1.0 ppm Cl_2 gas was measured, respectively.

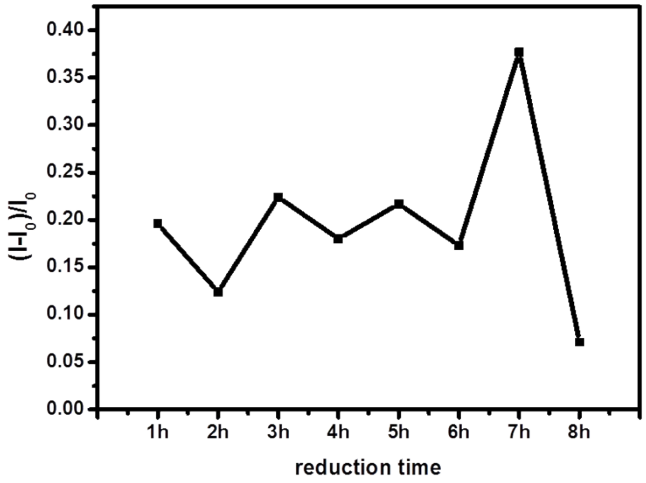


Figure S6. The effect of GO reduction time on the relative conductance response of rGO-$BmimBF_4$ towards 1 ppm of Cl_2. The variation of conductance response is irregular, which may only ascribed to the accidental error during detection

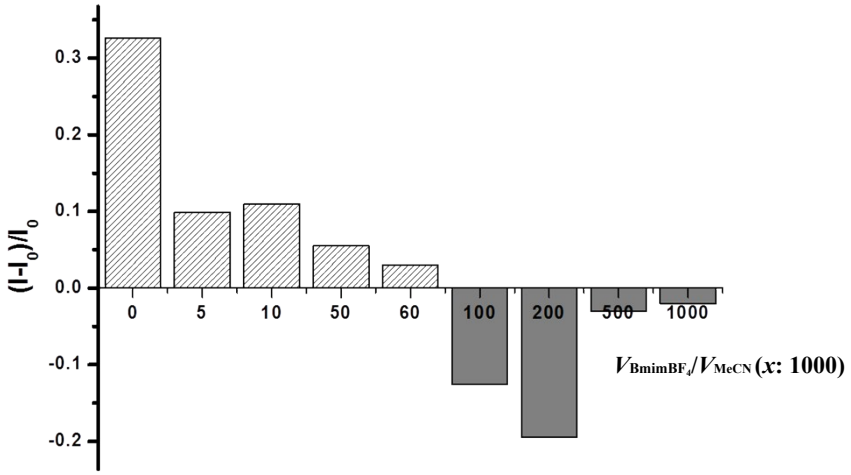


Figure S7. The effect of rGO/$BmimBF_4$ ratio on the relative conductance response the paper supported rGO-$BmimBF_4$ to 1 ppm Cl_2. The paper chip was obtained by filtrating around 500 μL of GO sol(2 mg/ml) through each of sensing area. Afterwards, the GO retained on the cellulose network was reduced by hydrazine hydrate steam at 90℃ for 3 hours. The rGO on different sensing spot was then modified with different amount of ionic liquids (ILs) by filtering $BmimBF_4$/ MeCN solution with different volume ratio through each sensing area.

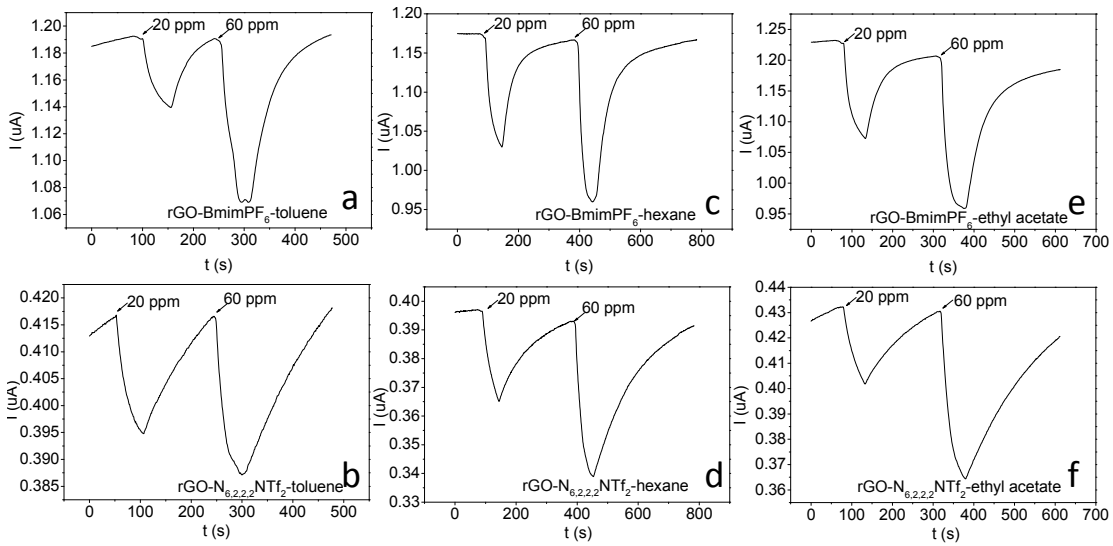


Figure S8. The conductance response of the paper-supported rGO-$BmimPF_6$ chip towards: (a) toluene; c) hexane; e) ethyl acetate. The conductance response of the paper-supported rGO-$N_{6,2,2,2}NTf_2$ chip towards: b) toluene; d) hexane; f) ethyl acetate. Each types of organic vapor were diluted with N_2 gas with an automatic gas calibrator system.

.

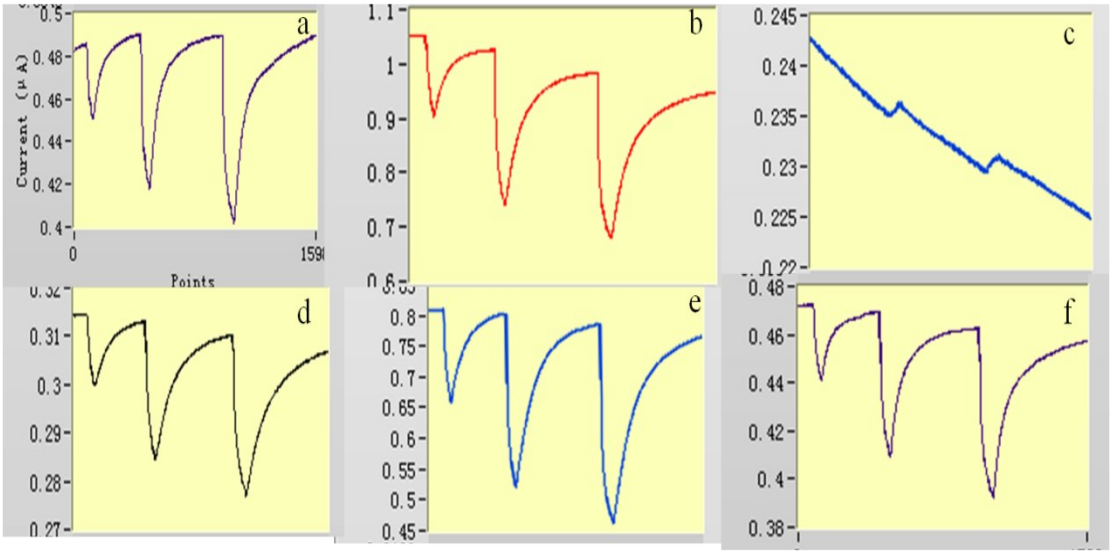


Figure S9. The conductance response on six sensing elements towards oxygen. The data were acquired by Labview software, the six sensing elements include: a) rGO-BmimOTf; b) rGO-$N_{6,2,2,2}NTf_2$; c) rGO; d) rGO-$BmimBF_4$; e) rGO-$BmimClO_4$; f) rGO-$BmimPF_6$.

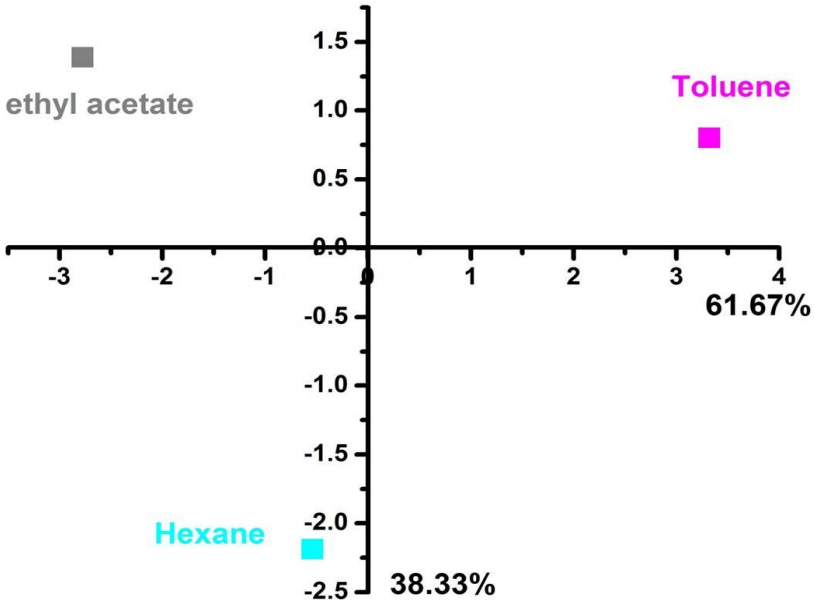


Figure S10. Two-dimensional PCA plot obtained from the normalized responding slopes of rGO-IL sensor array in response to three types of VOC samples. Before the PCA analysis, the data from inorganic gases were excluded.

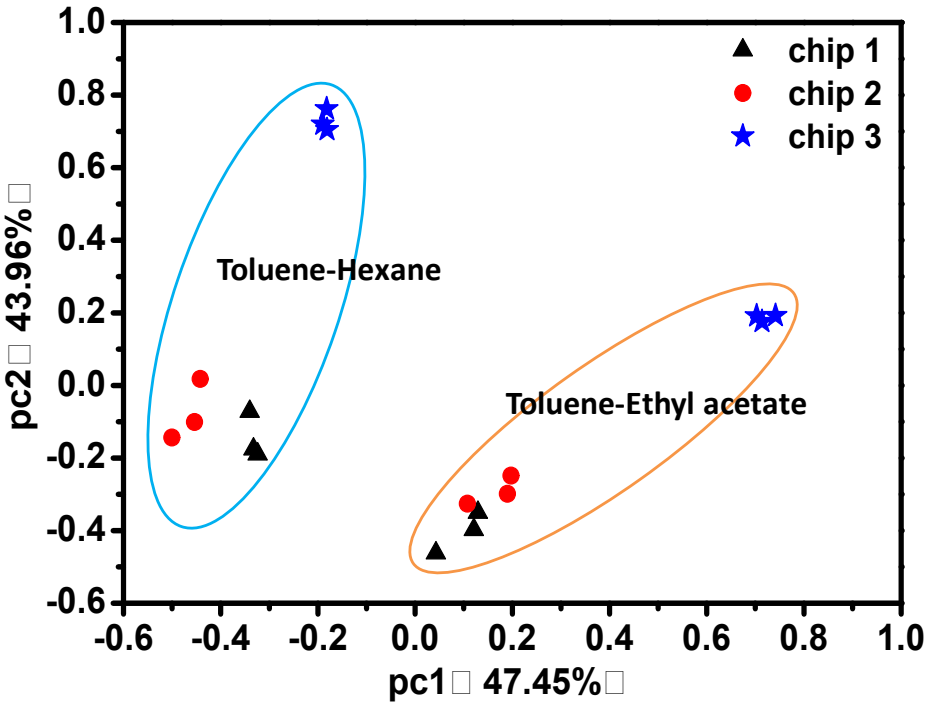
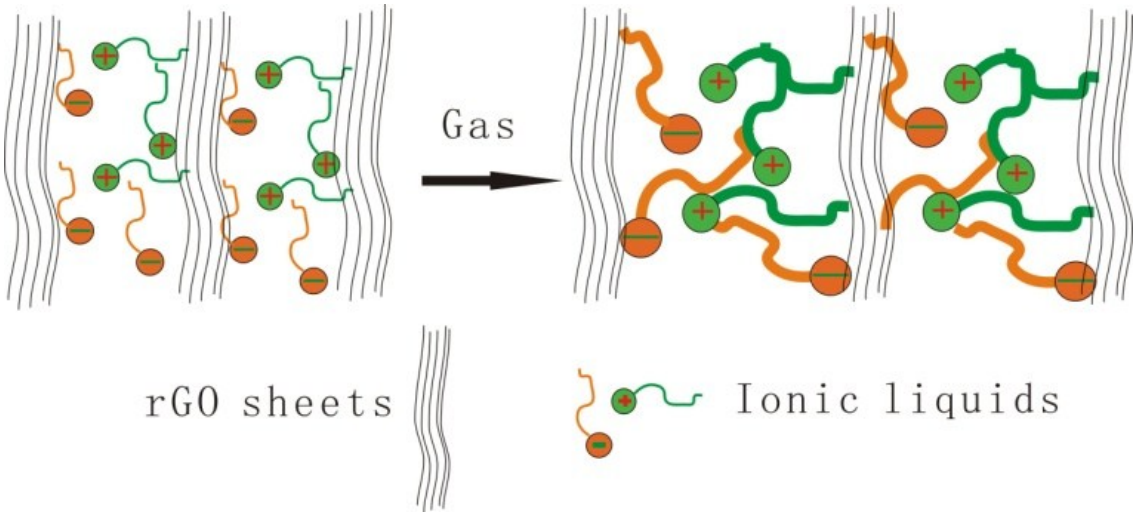


Figure S11. Two-dimensional PCA plot obtained from the normalized responding signals of rGO-IL sensor array in response to two types of mixed gas sample. The data points assigned with different color were obtained on three paper chip prepared with same methods, respectively. For each gas sample, three parallel detections were performed on a paper chip. Toluene-hexane mixture and Toluene-ethyl acetate mixture can be well discriminated in the PCA plot, indicating that the sensor array is selective to the VOC components. The data point obtained on a same paper chip is highly repeatable. However, dispersion of data point can be found on different paper chip due to the batch to batch variation in chip preparation.



Scheme S1. The schematic illustrating the inter-sheet mechanism of rGO-IL in response to VOCs. When VOCs were adsorbed by ILs, the distance between rGO sheets(δ) and dielectric constant(ε_r) will accordingly change, resulting in the decrease of electron hopping ability and consequently the reduction of conductance response.