Supplementary Information

The role of anion and cation in the gas sensing mechanisms of graphene decorated with lead halide perovskite nanocrystals

Juan Casanova-Chafer, [†a] Rocio Garcia-Aboal, [†b] Pedro Atienzar [*b] and Eduard Llobet [*a]

[a.] MINOS, Universitat Rovira i Virgili, 43007 Tarragona, Spain.
[b.] Instituto de Tecnología Química, CSIC-UPV, Universitat Politècnica de València, 46022 Valencia, Spain.
E-mail: pedatcor@itq.upv.es and eduard.llobet@urv.cat
[†] Authors that contributed equally to the work.

Text S1. Perovskite nanocrystal syntheses.

It is well-known that lead halide perovskites present the following configuration: **ABX_3**. Where **B** is the Pb^{+2}, **A** corresponds to an organic or inorganic cation, in our case we employed MA ($CH_3NH_3^+$), FA (($NH_2)_2CH^+$) and caesium (Cs^+). Meanwhile, **X_3** represents the anion, in our work we used Cl^-, Br^- and I^-. To obtain the different perovskite nanocrystals, different synthesis routes were followed:

$MAPbX_3$ (where X = Br^-, Cl^-, I^-): the synthesis of perovskite NCs having MA cation was adapted from the method proposed by L. Schmidt et al[1]. First, a common solution for the next step was prepared, 85 mg of oleic acid (OA) were added to 2 mL of 1-octadene (ODE). The solution was stirred and heated to 80°C. Afterwards, 33.5 mg of octylammonium bromide (OABr) were added.

Then, another specific solution was prepared for each perovskite anion by using different precursors. In the case of $MAPbBr_3$ nanocrystals, 26.4 mg and 18.3 mg of methylammonium bromide (MABr) and lead (II) bromide ($PbBr_2$) respectively, were dissolved in 200 μL of Dimethylformamide (DMF). Meanwhile, 3.37 mg and 13.9 mg of methylammonium chloride (MACl) and lead (II) chloride ($PbCl_2$) respectively, were dissolved in 200 μL of Dimethylsulfoxide (DMSO) to form $MAPbCl_3$. Lastly, to prepare the $MAPbBr_{2.5}I_{0.5}$ nanocrystals, 2.7 mg, 3 mg and 18.5 mg of methylammonium iodine (MAI), methylammonium bromide (MABr) and lead (II) bromide ($PbBr_2$) respectively, were added to 300 μL of DMF. The solutions were stirred until complete dissolution.

Finally, each solution with the specific precursors was added to the first reported solution. Then, the solutions were cooled to 60°C and 5 mL of acetone were added, inducing the immediate precipitation of the different nanocrystals. In fact, a yellow, white and yellow-orange precipitates were obtained for $MAPbBr_3$, $MAPbCl_3$ and $MAPbBr_{2.5}I_{0.5}$ respectively. Then, the solutions were centrifugated at 6000 rpm for 10 minutes in order to extract the precipitates. Afterwards, the precipitates were dispersed in Toluene.

$CsPbBr_3$: for the synthesis of this type of nanocrystals was followed the method proposed by L. Protesescu et al[2]. To prepare the Cs-oleate, a 3-neck flask was loaded with Cs_2CO_3 (814 mg), ODE (40 mL) and OA (2.5 mL). Then, the solution was mixed under stirring and was heated to 120°C for 1 hour. Afterwards, the temperature was increased up to 150°C under a nitrogen atmosphere to ensure the complete reaction of Cs_2CO_3 with the oleic acid. Then, the solution was cooled to room temperature, obtaining a precipitate of Cs-oleate.

Subsequently, another solution was prepared by mixing 69 mg of $PbBr_2$ and 5 mL of ODE in a 3-neck flask. Continuously, the solution was dried under vacuum at 120°C for 1 hour. Then, 0.5 mL of dried oleylamine (OLA) and OA were injected meanwhile a nitrogen atmosphere was created. After complete solubilization, the temperature was raised to 140°C and Cs-oleate solution (0.4 mL, preheated to 100°C before injection) was quickly injected. Five seconds later, the final solution was cooled down by using an ice-water bath. Finally, 5 mL of Tert-butyl alcohol (tBuOH) was added to help the complete NCs precipitation. After the centrifugation step reported in the previous synthesis, the $CsPbBr_3$ NCs were redispersed in hexane.

$FAPbBr_3$: NCs containing FA cation were prepared following the method proposed by L. Protesescu et al[3]. First, FA-oleate precursor was prepared, where a 3-neck flask was loaded with 521 mg of formamidinium acetate (FA(CH_3COO)) and 20 mL of OA in order to prepare the FA-oleate. Then, similarly to the above synthesis, the solution was heated to 120°C for 1 hour.

Subsequently, the temperature was increased up to 130°C until the complete reaction. Then, the FA-oleate was dried for 30 min at 50°C under vacuum and finally cool to room temperature.

Then, other solution was prepared by mixing ODE (5 mL) and $PbBr_2$ (69 mg) in a 3-neck flask. The solution was continuously dried under vacuum for 1 hour at 120°C. Afterwards, 0.5 mL of OLA and 1 mL of OA were injected at 120°C under nitrogen flow. After complete solubilization of the $PbBr_2$ salt, the temperature was lowered to 100°C. Then, 2.5 mL of FA-oleate solution was quickly injected and, 5 sec later, the reaction mixture was cooled by using an ice-water bath. Finally, 10 mL of toluene and 5 mL of acetonitrile were added to help the complete precipitation of NCs. Finally, the solution was centrifugated and the $FAPbBr_3$ NCs were redispersed in hexane.

In order to clarify the different synthesis, a summary is added:

Perovskite	Precursors	Synthesis Reagents	Solvent	Solvent Stabilizer
$MAPbBr_3$	26.4 mg MABr 18.3 mg $PbBr_2$	85 mg OA 2 mL ODE 33.5 mg OABr	5 mL Acetone 200 µL DMF	Toluene
$MAPBCl_3$	3.37 mg MACl 13.9 mg $PbCl_2$	85 mg OA 2 mL ODE 33.5 mg OABr	5 mL Acetone 200 µL DMSO	Toluene
$MAPbBr_{2.5}I_{0.5}$	2.7 mg MAI 3 mg MABr 18.5 mg $PbBr_2$	85 mg OA 2 mL ODE 33.5 mg OABr	5 mL Acetone 300 µL DMF	Toluene
$CsPbBr_3$	814 mg Cs_2CO_3 69 mg $PbBr_2$	45 ml ODE 2.5 mL OA 0.5 mL OLA	5 mL tBuOH	Hexane
$FAPbBr_3$	521 mg $FA(CH_3COO)$	21 mL OA 5 mL ODE 0.5 mL OLA	10 mL Toluene 5 mL Acetonitrile	Hexane

Text S2. Graphene decoration with perovskite NCs and gas sensing set-up.

Once the different perovskite NCs were synthesized, a graphene solution in toluene or hexane (0.5 mg/mL) was prepared by using graphene nanoflakes from Strem Chemicals, Inc. (US). Afterwards, the solution was placed in an ultrasonic tip to apply a pulsed sonication (1s on/2s off) at 280 W for 90 minutes. Then, once the graphene is properly exfoliated, perovskite NCs were added (5% wt.) to the solution and the nanomaterials were mixed in an ultrasonic bath for 1 hour. Finally, the resulting graphene flakes decorated with perovskite NCs were deposited onto alumina substrates that comprised screen-printed platinum interdigitated electrodes by a spray pyrolysis technique.

It is important to note that the preparation of graphene has an essential role in gas sensing performance. In this paper, the lead halide perovskite nanocrystals are supported on liquid-phase exfoliated (LPE) graphene, an attractive preparation method given its low cost. It can be foreseen that higher responses could have been reached using more costly graphene, e.g. mechanically exfoliated graphene[4] or chemical vapor deposited (CVD). However, this general improvement in responsiveness would have not affected the relative performance of the anions/cations in lead halide perovskites.

The sensors developed were placed in an airtight Teflon chamber with a volume of 35 cm^3, which is connected to calibrated gas cylinders with pure dry air (Air Premier Purity: 99,995%) and the different gases tested. Then, different dilutions of target gases were performed in order to obtain different concentrations. The sensors were stabilized under synthetic dry air for 5 minutes before the application of the target gas concentration during 1 min of exposure. The total flow was adjusted to 100 mL/min using a set of Bronkhorst High-Tech B.V. (Ruurlo, The Netherlands) mass-flows controllers. And the resistance changes were registered using an Agilent HP 34972A multimeter connected to the test chamber. The responses were defined as ($\Delta R/R_0$) expressed in percentage. Where ΔR is the resistance change over one minute of gas exposure, meanwhile R_0 corresponds to the baseline resistance.

Figure S1. High-Resolution Transmission Electron Microscope (HRTEM) images of MAPbBr$_3$ (a), CsPbBr$_3$ (b), FAPbBr$_3$ (c), MAPbCl$_3$ (d) and MAPbBr$_{2.5}$I$_{0.5}$ (e) perovskite NCs.
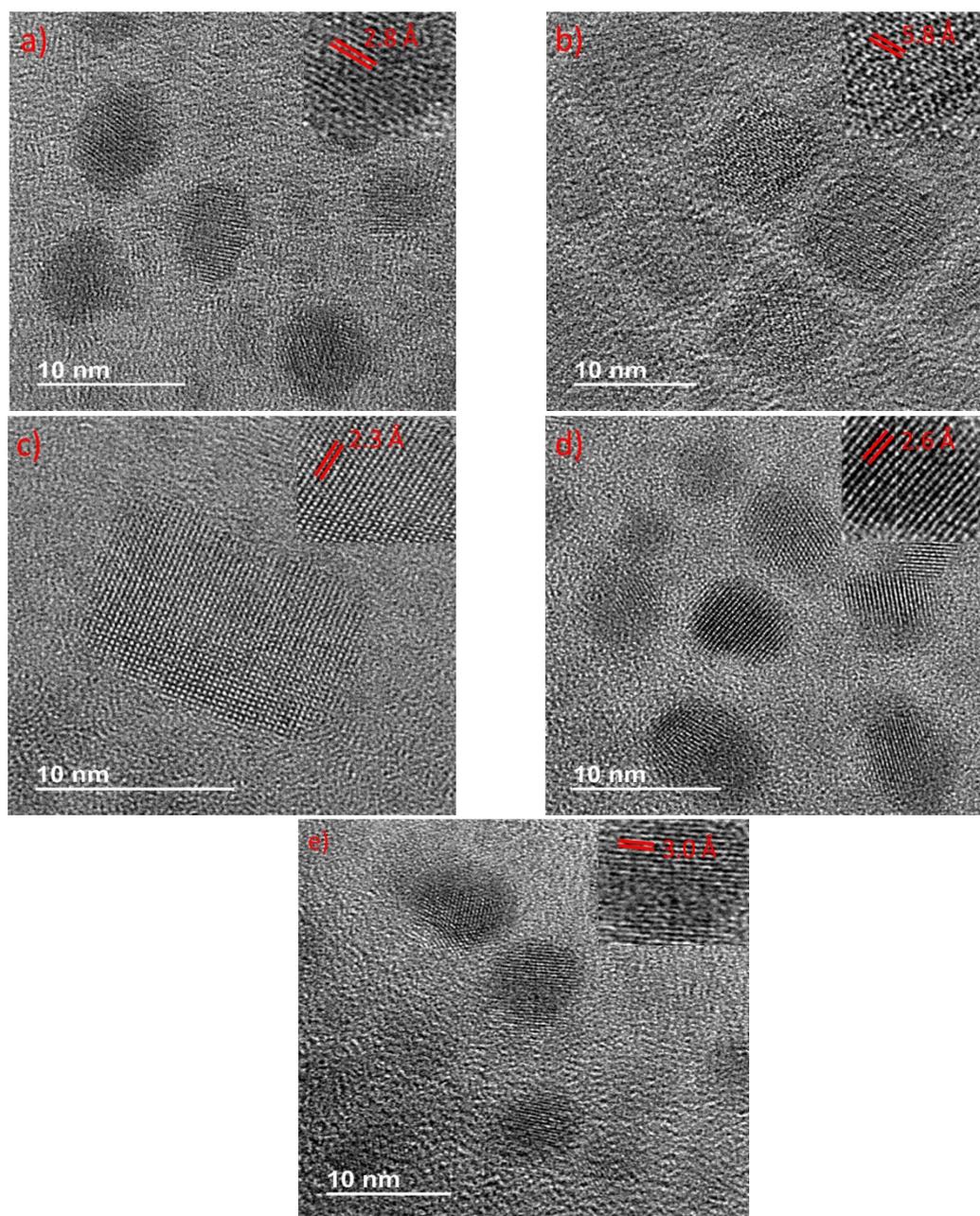
Table S1. Data extracted from the HRTEM images (Fig. S1).

Perovskite NCs	Average size (nm)	Interplanar distance (Å)
MAPbBr$_3$	7.2 ± 2.2	2.8
CsPbBr$_3$	8.7 ± 1.1	5.8
FAPbBr$_3$	6.9 ± 1.2	2.3
MAPbCl$_3$	5.6 ± 1.5	2.6
MAPbBr$_{2.5}$I$_{0.5}$	6.3 ± 0.6	3.0

Figure S2. X-Ray Diffraction (XRD) patterns for the different perovskite structures.
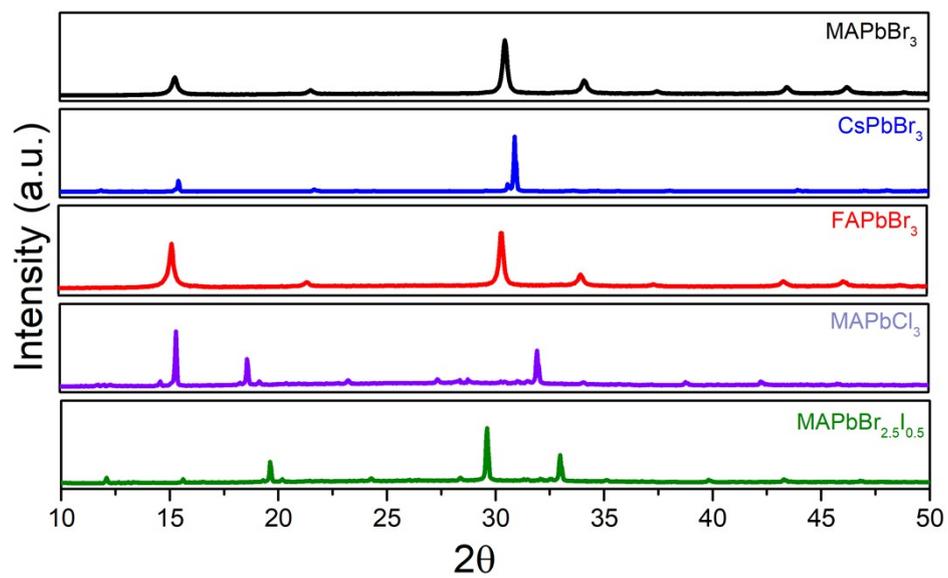
Figure S3. Field Emission Scanning Electron Microscope (FESEM) image showing the sensor surface (a), and image recorded with Back-Scattered Electron (BSE) detector (b). In this case, the bright spots correspond to the perovskite NCs, meanwhile, black background corresponds to graphene.
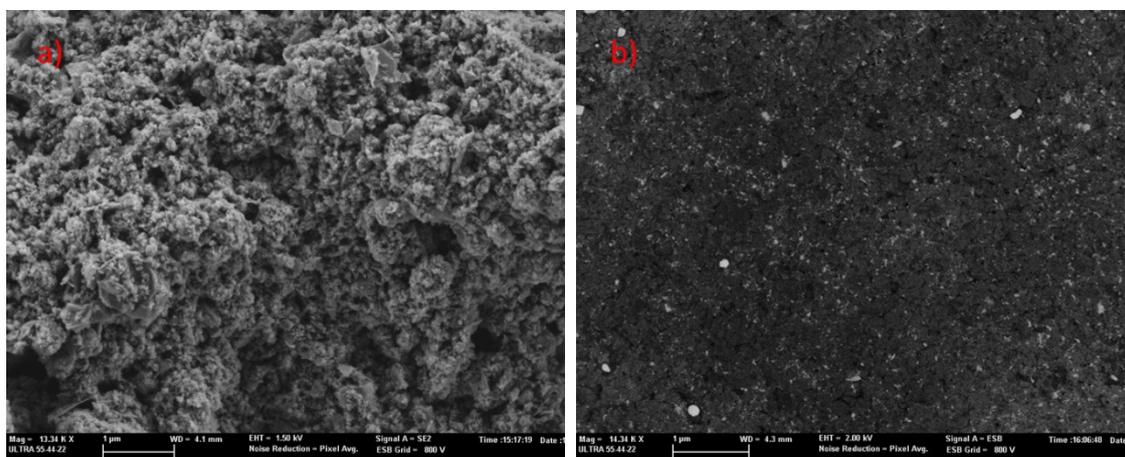
Figure S4. Graphene decorated with perovskite NCs layer deposited onto alumina substrate (a), and gas sensing chamber used (b).
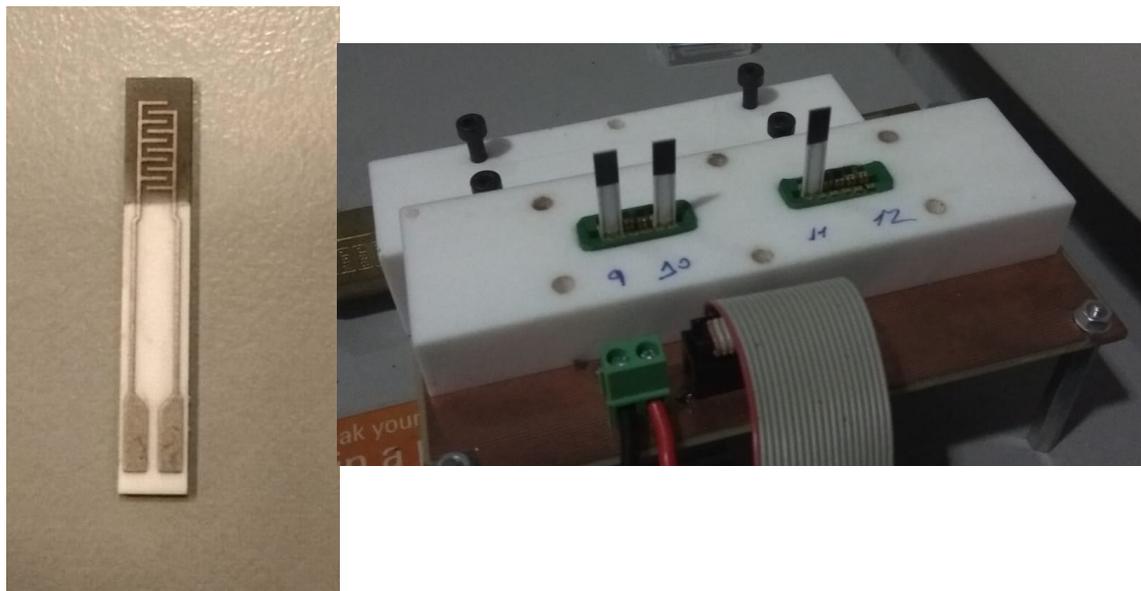
Figure S5. Responses obtained for benzene and toluene using graphene decorated with different perovskite NCs. For the two vapours, 2, 4, 6 and 8 ppm were applied in three consecutive cycles.

Perovskite NCs	Benzene	Toluene
MAPbBr$_3$		
CsPbBr$_3$		
FAPbBr$_3$		
MAPbCl$_3$		
MAPbBr$_{2.5}$I$_{0.5}$		
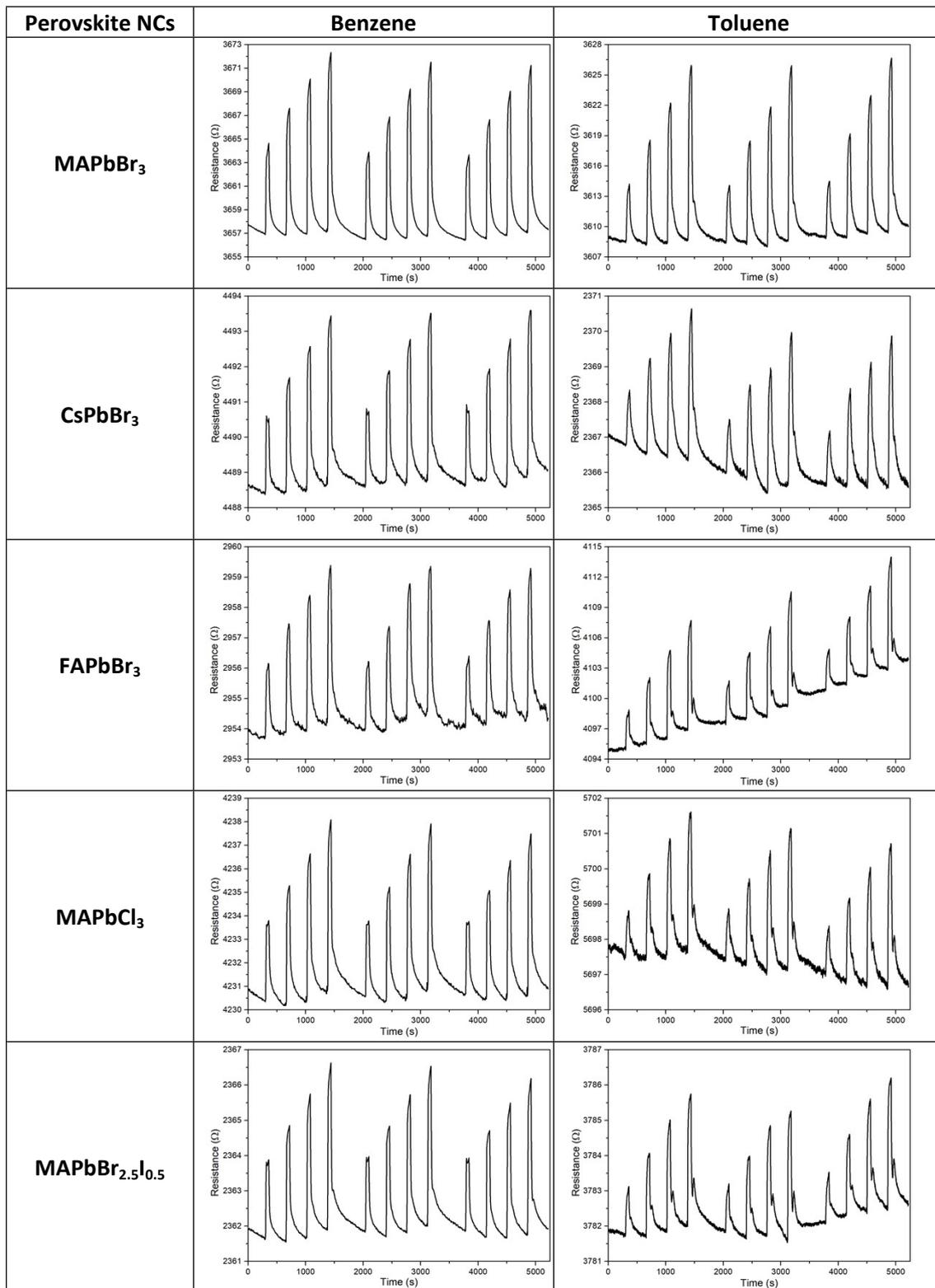
Figure S6. Zoom of the graph shown in Figure 2a. In particular, the present graph shows the resistance changes (black line) for graphene decorated with MAPbBr$_3$ NCs under the exposure to increasing concentrations of benzene (red dashed line).
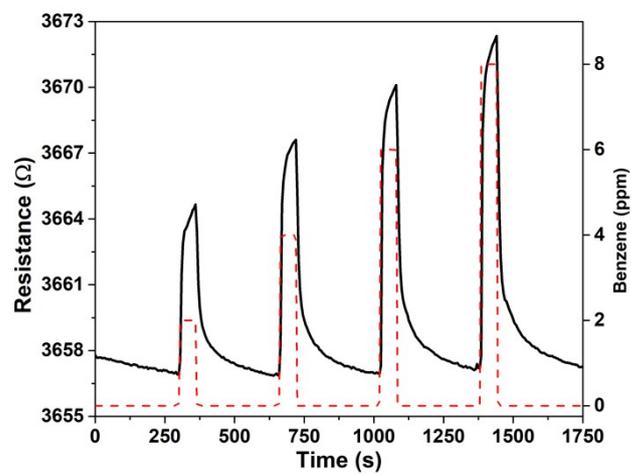
Table S2. Example of the average responses of graphene decorated with the different perovskite NCs towards benzene exposure.

C_6H_6 (ppm)	MAPbBr$_3$	FAPbBr$_3$	MAPbBr$_{2.5}$I$_{0.5}$	MAPbCl$_3$	CsPbBr$_3$
2	0.202 ± 0.007	0.079 ± 0.004	0.096 ± 0.004	0.080 ± 0.005	0.0472 ± 0.0001
4	0.283 ± 0.008	0.117 ± 0.004	0.139 ± 0.006	0.119 ± 0.006	0.070 ± 0.001
6	0.345 ± 0.012	0.147 ± 0.006	0.172 ± 0.006	0.149 ± 0.004	0.0904 ± 0.0005
8	0.402 ± 0.014	0.167 ± 0.007	0.197 ± 0.007	0.169 ± 0.005	0.104 ± 0.001

The measurement methodology used in this work results in highly reproducible (less than 5% of error), reversible (absence of significant baseline drift) and fast (1-minute exposure) responses at room temperature. A similar strategy has been reported by many authors[5–7], in which the measurements outside the steady-state regime enable achieving representative calibration curves with a low operating cost.

However, since the sensor behaviour during gas exposure until stabilization of the response is important, Figure S7 shows the sensor saturation and its baseline recovery. The response and recovery times (t90) are about 30 min for a flow rate of 400 mL/min.
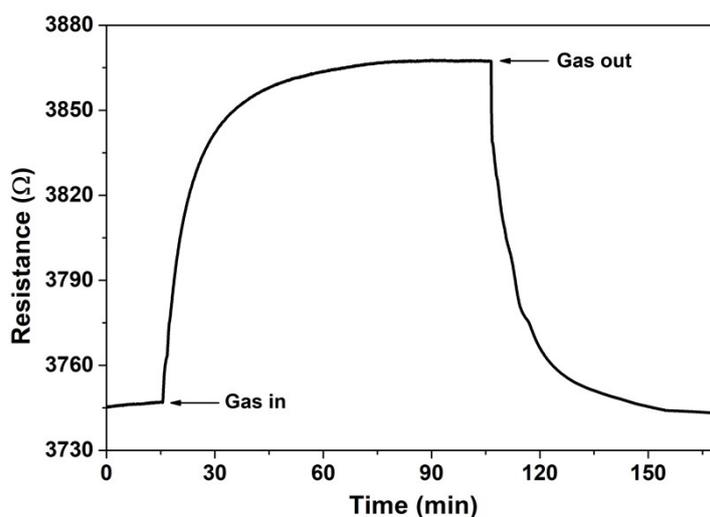
Figure S7. Typical response and recovery curve for a lead halide perovskite loaded graphene sensor operated at room temperature. Once the resistance baseline was stable in dry air, 10 ppm of toluene were applied until reaching the saturation of sensor response. Baseline recovery was achieved in pure air.

Figure S8. Reproducibility analysis using the MAPbBr$_3$ perovskite. Resistance changes (black line) under exposure to 10 ppm of benzene (red line) for long times (30 minutes) were registered.
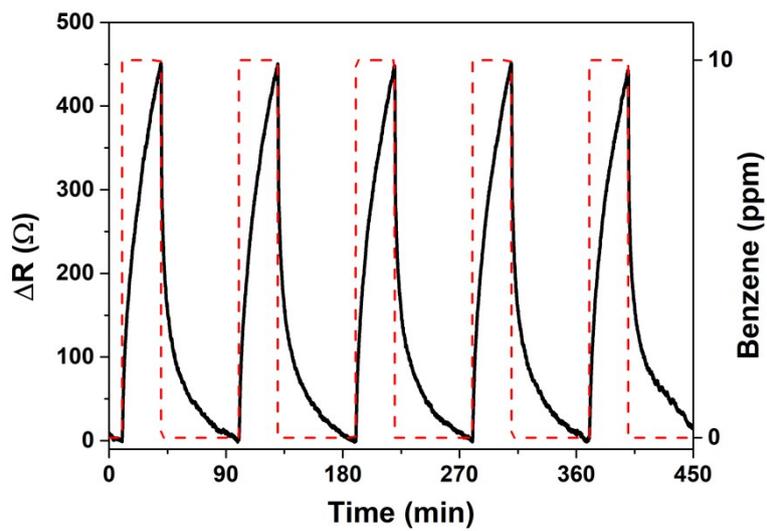
Figure S9. Comparison between the sensor signals registered for bare graphene (red line and right y-axis) and graphene decorated with MAPbBr$_3$ NCs (black line and left y-axis). The resistance changes correspond to one-minute exposures for 2, 4, 6 and 8 ppm of benzene during three consecutive, replicate cycles.
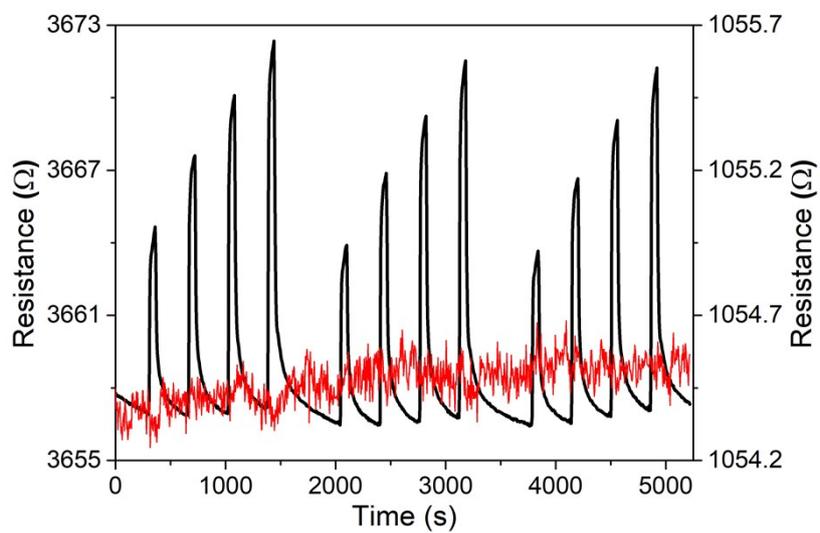
Figure S10. Calibration curves obtained for toluene detection using lead halide perovskites with different cation (a) and anion (b).
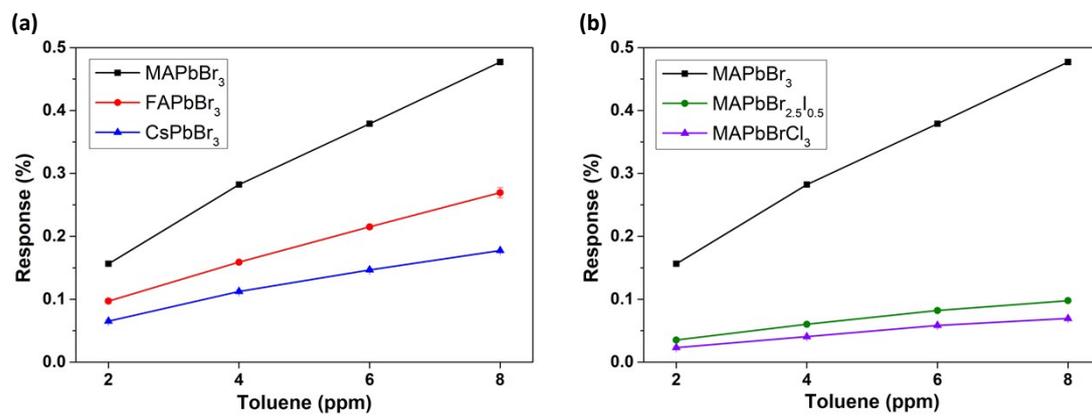
Figure S11. (a) Examples of electrical response to NO_2 using $FAPbBr_3$. Three consecutive, replicate cycles with four concentrations (250, 500, 750 and 1000 ppb) were applied for 1-minute exposure. Pure dry air was used for a five-minute cleaning between the different concentrations tested. (b) Gas exposure to different concentrations of NH_3 by using graphene decorated with $FAPbBr_3$ NCs. No sensitivity to ammonia was obtained because the resistance changes recorded remain almost identical for the different analyte concentrations. (c) Comparison of the electrical responses to NH_3 using $MAPbCl_3$ (black line) and $MAPbBr_3$ (red line). Three consecutive cycles with four concentrations (25, 50, 75 and 100 ppm) were applied for one minute. Again, five-minute cleaning in dry air periods were applied between ammonia exposures.

15
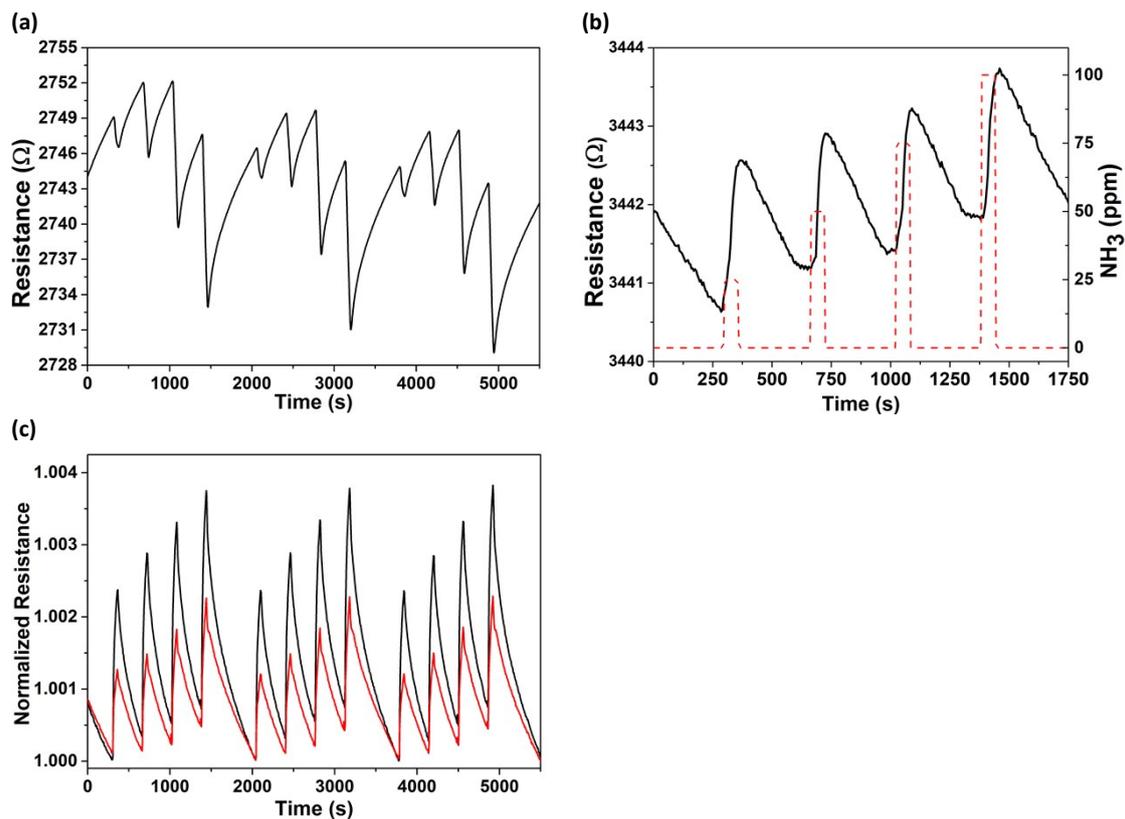
References

1   L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Mínguez Espallargas, H. J. Bolink, R. E. Galian and J. Pérez-Prieto, *J. Am. Chem. Soc.*, 2014, **136**, 850–853.

2   L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692–3696.

3   L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Bertolotti, N. Masciocchi, A. Guagliardi and M. V. Kovalenko, *J. Am. Chem. Soc.*, 2016, **138**, 14202–14205.

4   F. Ricciardella, S. Vollebregt, T. Polichetti, M. Miscuglio, B. Alfano, M. L. Miglietta, E. Massera, G. Di Francia and P. M. Sarro, *Nanoscale*, 2017, **9**, 6085–6093.

5   F. Auerbach, in *International Conference on Solid-State Sensors and Actuators, and Eurosensors IX, Proceedings*, IEEE, 1995, **1**, 791–794.

6   N. El Barbri, C. Duran, J. Brezmes, N. Cañellas, J. Ramírez, B. Bouchikhi and E. Llobet, *Sensors*, 2008, **8**, 7369–7379.

7   V. Martini, S. Bernardini, M. Bendahan, K. Aguir, P. Perrier and I. Graur, in *Sensors and Actuators, B: Chemical*, Elsevier, 2012, **170**, 45–50.