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# Cation-Anion Influence in Lead Halide Perovskites Supported on Graphene for $NH_3$ Detection

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## Summary:

Chemiresistive sensors offer a promising option for establishing extensive sensing networks, providing a cost-effective and energy-efficient solution. This study introduces novel hybrids consisting of lead halide perovskite nanocrystals decorating graphene, operable under ambient temperature conditions. Evaluating the impact of two cations (methylammonium and cesium) and two anions (chlorine and bromine), $MAPbBr_3$ emerges as the most promising composition for $NH_3$ detection at room temperature.

**Keywords:** gas sensor, $NH_3$ detection, chemical resistive sensor, graphene, lead halide perovskites

## Background, Motivation an Objective

In recent decades, the escalating threat of air pollution has underscored the urgent need for continuous monitoring to safeguard both the environment and public health. However, establishing a large air quality sensor network requires reliable, cost-effective, and energy-efficient sensing devices. Chemiresistive sensors, owing to their simple fabrication and operation, emerge as a promising option. Graphene has garnered considerable attention, albeit with limited gas sensitivity and selectivity owing to its inherent chemical inertness [1].

In response to this challenge, significant research efforts have shifted towards leveraging perovskites for gas sensing applications. Perovskites offer advantages such as room-temperature operation and tunable bandgap. Despite their promise, perovskites suffer from instability in humid conditions, limiting their commercial viability. Recent studies have demonstrated that dispersing perovskite nanocrystals on graphene effectively shields them from ambient moisture, thus mitigating long-term degradation [2].

This advancement suggests that decorating graphene with perovskite nanocrystals (NCs) holds immense potential for developing gas sensors that are both sensitive and selective, while also being cost-effective and energy-efficient.

## Method

The influence of both anions and cations in lead halide perovskites for $NH_3$ detection has been investigated for the first time. The perovskite composition significantly affects sensing performance. Lead halide perovskites are typically structured as $ABX_3$, with B representing $Pb^{+2}$ and A representing a cation. In this study, an organic methylammonium (MA+) and an inorganic cesium (Cs+) were utilized as cations. The $X_3$ denotes the anion, with $Cl^-$ and $Br^-$ being employed. Various synthesis methods, as outlined in our previous publication [3], were employed to obtain different compositions ($MAPbBr_3$, $MAPbCl_3$, and $CsPbBr_3$).

Briefly, for $MAPbX_3$ (where X = $Br^-$, $Cl^-$), the synthesis included preparing solutions of oleic acid (OA), 1-octadene (ODE), and octylammonium bromide (OABr). Specific solutions for each perovskite anion were then prepared using different precursors for $Br^-$ (MABr and $PbBr_2$) and $Cl^-$ (MACl and $PbCl_2$) anions. These solutions were combined, cooled, and acetone was added to induce nanocrystal precipitation.

After centrifugation, the precipitates were dispersed in toluene. For $CsPbBr_3$, Cs-oleate was prepared by mixing $Cs_2CO_3$, ODE, and OA in a heated flask. Another solution, consisting of $PbBr_2$ and ODE, was prepared, dried, and injected with oleylamine (OLA) and Cs-oleate. After solubilization, the solution was cooled, and tert-butyl alcohol (tBuOH) was added for precipitation. The resulting $CsPbBr_3$ nanocrystals were redispersed in hexane after centrifugation.

Subsequently, a graphene solution underwent pulsed sonication (1s on/2s off) at 280 W for 90 minutes to ensure proper exfoliation. The perovskite NCs were then added (5% wt.) to the solution, and the mixture was vigorously stirred for 1 hour. The resulting hybrids were deposited onto alumina substrates containing screen-printed platinum interdigitated electrodes. The developed sensors were enclosed in an airtight Teflon chamber connected to calibrated gas cylinders.

## Results

Various dilutions of $NH_3$ with dry air were prepared to achieve different concentrations (25, 50, 75, and 100 ppm). Before exposure to the target gas concentration for 5 minutes, the sensors were stabilized under synthetic dry air for 15 minutes. The sensors were tested at room temperature to minimize power consumption, extend the active nanomaterials' lifetime, and prevent perovskite degradation.

Fig. 1 depicts electrical responses recorded upon $NH_3$ exposure during cycles, illustrating a high level of reversibility in the interaction, almost fully recovering the initial baseline resistance. Additionally, despite operating in dynamic mode, the sensors exhibited high repeatability.

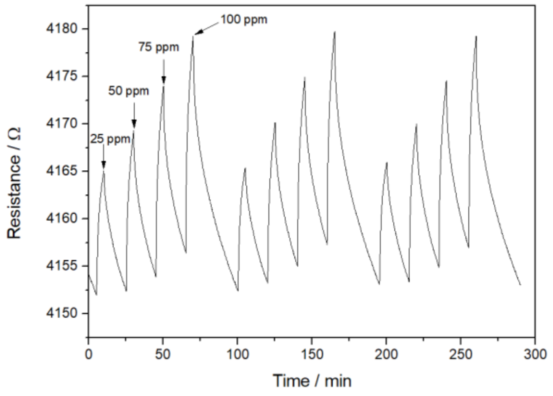

*Fig. 1. Example of the electrical responses using $MAPbBr_3$ NCs decorating graphene to detect four concentrations (25, 50, 75 and 100 ppm) of $NH_3$ during 3 consecutive cycles.*

Fig. 2 compares the sensing performance of the different hybrids in detecting $NH_3$. Several conclusions can be drawn. Firstly, bare graphene exhibited lower responses to $NH_3$ compared to decorated graphene, indicating that the presence of perovskite nanocrystals (NCs) on graphene enhances sensitivity to the target gas, regardless of perovskite composition.

Secondly, among the various perovskites employed, $MAPbBr_3$ demonstrated notably better sensing responses than $MAPbCl_3$ and $CsPbBr_3$. Specifically, for 100 ppm of $NH_3$, $MAPbBr_3$ NCs exhibited approximately three times higher responses than the other perovskite compositions. This suggests that $MAPbBr_3$ likely possesses an optimal energy-level alignment with graphene for hole extraction, as the hybrids function as p-type semiconductors for electron donor gases like $NH_3$.

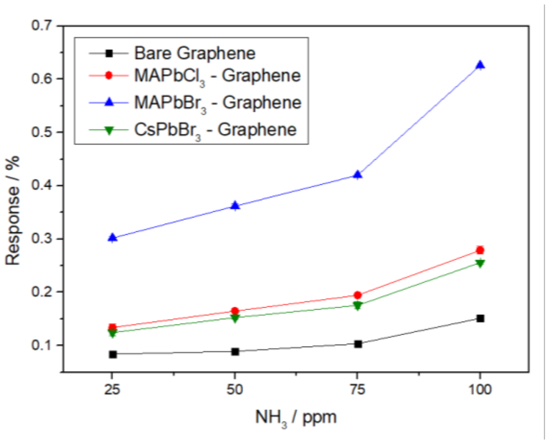

*Fig. 2. Calibration curves comparing 4 sensor compositions for detecting $NH_3$.*

Moreover, $MAPbBr_3$ tends to feature a higher density of trap states compared to $MAPbCl_3$ and $CsPbBr_3$, which could potentially interact with gas compounds. Furthermore, experimental findings reveal that $MAPbBr_3$ exhibits a lower photoluminescence quantum yield, indicating a higher concentration of defects that may also facilitate interaction with $NH_3$.

## References

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