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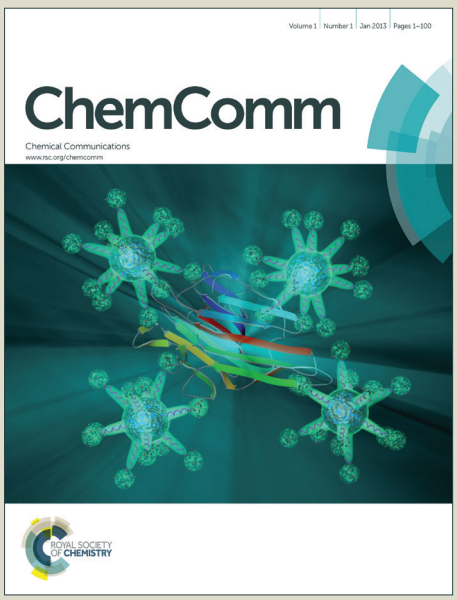

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A resistance change effect in perovskite $CH_3NH_3PbI_3$ films induced by ammonia

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The resistance of the perovskite $CH_3NH_3PbI_3$ film was found to decrease significantly in seconds when the film exposed in the NH_3 atmosphere at room-temperature, and recover to its original value in seconds when out of NH_3 environment.

Organometal halide perovskites such as $CH_3NH_3PbX_3$ (X = Cl, Br, I) have recently attracted much attention as light-harvesting materials for solar cells,[1-5] owing to their appropriate direct bandgap, large absorption coefficient,[6,7] long carrier lifetime and high carrier mobility.[8,9] The power conversion efficiency of perovskite solar cells has been rapidly boosted from 3.8% to 20.1%.[1,10] In recent two years, organometal halide perovskites also showed attractive application prospect in photodetectors,[11,12] light emitting diodes,[13-15] and lasers.[16,17] Generally this class of compounds very easily absorb polar gases and vapor, which is considered to be a critical factor detrimentally affecting the long-term stabilities of perovskite devices.[18] Interestingly, however, one can take advantage of this feature of these materials to extend their applications as gas sensors. Zhu's group found that the color of perovskite $CH_3NH_3PbI_3$ ($MAPbI_3$)/TiO_2 film changed from brown to colorless immediately (<1 s) when exposed in the NH_3 atmosphere, and turned back to the original color within seconds after removed from NH_3, suggesting its application for NH_3 sensor. However, they also found that the perovskite $MAPbI_3$/TiO_2 film exposed to NH_3 for a long period of time (tens of minutes) could not turn back to brown color when the NH_3 atmosphere removed.[19] The poor stability and repeatability will seriously hinder the application of perovskite in optical-based NH_3 sensors.

In this work, we investigated the resistance change of perovskite $MAPbI_3$ film induced by NH_3. We found that the resistance of the perovskite $MAPbI_3$ film was obviously reduced within seconds when the film was exposed in the NH_3 atmosphere and the film could return to the high resistance state within seconds after the NH_3 atmosphere was removed. Our study indicated that a new phase has been produced after the perovskite $MAPbI_3$ react with NH_3, and the resistance of the new phase showed similar sensitive response to NH_3 as perovskite $MAPbI_3$. These phenomena inspire the new application of perovskite as electrical-based NH_3 sensors with higher stability than optical-based NH_3 sensors. Besides, the insight to the interacting of $MAPbI_3$ with the surrounding environment in our study could also inspire the work to improve the long-term stability of devices based on this class of perovskite materials.

$MAPbI_3$ film was fabricated by the one-step spin-coating method according to the work reported elsewhere previously.[20] Briefly, FTO glass was patterned by laser cutting and cleaned with acetone, ethanol and deionized water respectively. Then the pre-cleaned FTO electrode was spin-coated with the $MAPbI_3$ precursor solution (40 wt%, in N, N-dimethylformamide) at a rate of 2000 rpm for 30 s, followed by annealing at 100 °C for 15 min. The thickness of the as-prepared perovskite films was about 1 μm (Fig. S1 ESI†). The resistance change of the $MAPbI_3$ film induced by NH_3 was measured in a Teflon chamber (50 mL) at room temperature (RT, around 25 °C). During the test, dry pure NH_3 (1 L min^{-1}) and N_2 (2 L min^{-1}) were injected into the chamber. The schematic diagram of the perovskite $MAPbI_3$ electrode structure and the test system is shown in Fig. 1(a).

Fig. 1(b) gives the I-V curves of the $MAPbI_3$ electrode exposed in the atmosphere of N_2 (NH_3 OFF) and the mixed atmosphere of NH_3 and N_2 (NH_3 ON). We can see that, within the test bias voltage (-3 V to 3 V), the current through the $MAPbI_3$ film under NH_3 OFF was obviously smaller than that under NH_3 ON. This indicates that the resistance of the $MAPbI_3$ film can be greatly decreased when the film is exposed in the NH_3 atmosphere. The sheet resistance of the films were also measured with four probe method before and after exposed in

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†Electronic supplementary information (ESI) available: The cross section SEM image of the perovskite film, figure of sheet resistance measurement and resistance change induced by moisture. See DOI: 10.1039/ x0xx00000x

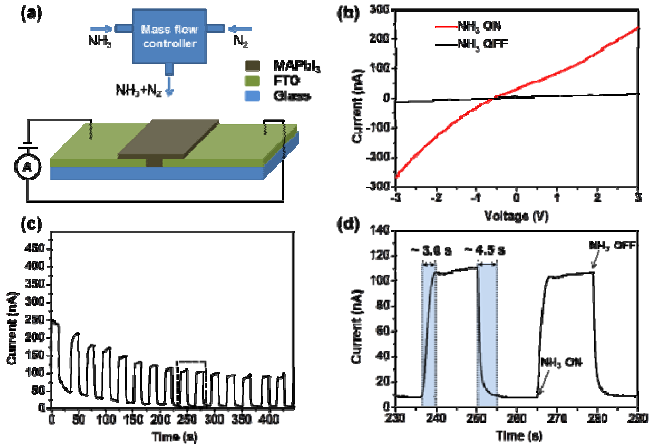

Fig. 1 (a) Schematic diagram of the $MAPbI_3$ film structure and the resistance measurement set-up. (b) I-V curves of the $MAPbI_3$ film when the NH_3 ON and OFF at RT. (c) I-t curve of the $MAPbI_3$ film with the NH_3 switching ON and OFF at RT. The applied bias voltage is 1.5 V. (d) The enlarged view of the dash line rectangle area in the I-t curve, which shows the current rise and decay when the NH_3 switching ON and OFF.

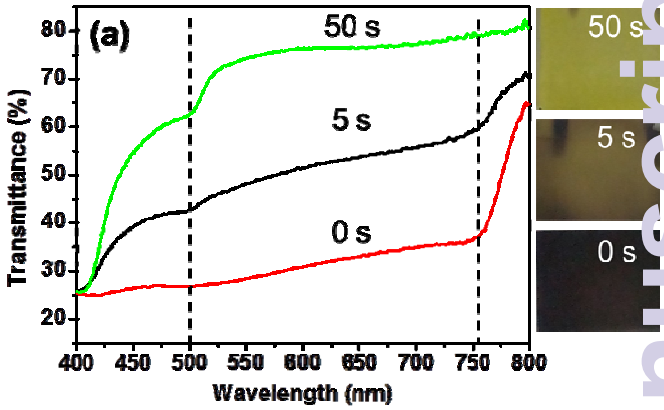

Fig. 2 Transmittance spectra (left) and the color change (right) of the perovskite $MAPbI_3$ film before (0 s) and after exposed in NH_3 atmosphere for 5 s and 50 s.

the NH_3 atmosphere. The results were shown in Fig. S2 (ESI†), which confirmed the resistance change of the film reduced by NH_3.

Fig. 1(c) shows the I-t curve of the $MAPbI_3$ film with the NH_3 flow switched ON and OFF. The current was tested under the bias voltage of 1.5 V. From the I-t curve we can see the current through the film under NH_3 ON was obviously greater than that under NH_3 OFF. At the beginning stage (before ~200 s) of the test, the measured currents under NH_3 ON and NH_3 OFF both decreased obviously. In order to explain this phenomenon, we speculate that there are two kinds of processes occurring when $MAPbI_3$ react with NH_3: one is reversible, such as adsorption or intercalation; and the other is an irreversible process. Reversible reaction is the reason why the resistance of the film can repeatedly response to the switch of NH_3: when the film is exposed in the NH_3 atmosphere, the NH_3 molecules will be adsorbed by the film or inserted in the space of the crystal lattice, and the film shows relatively low resistance; when the NH_3 atmosphere is removed, the NH_3 molecules adsorbed or inserted in the film will be quickly released, and the film returns to the relatively high resistance state. Meanwhile, NH_3 can also irreversibly transform perovskite $MAPbI_3$ into a new phase or compound (signed as $MAPbI_3$+NH_3). In the same environment (NH_3 ON or OFF), the resistance of the $MAPbI_3$+NH_3 film is higher than the pristine perovskite $MAPbI_3$ film, so at the beginning stage of the test, the measured currents when NH_3 is ON and OFF decrease obviously. At the last stage (after ~200 s) of the test, when the perovskite $MAPbI_3$ film is completely transformed into $MAPbI_3$+NH_3, both of the currents when the NH_3 is ON and OFF become relatively stable.

Both the pristine $MAPbI_3$ perovskite film and the newly generated $MAPbI_3$+NH_3 film show quick response to the NH_3. Fig. 1(d) shows that when the NH_3 switch from OFF to ON, the current increases from below 10 nA to the saturation current (~110 nA) in about 3.0 s. When the NH_3 is OFF, the current can recover to below 10 nA in about 4.5 s. This is a very short response time for NH_3 sensor, especially for sensors working at RT.[21,22] These results inspire the potential application in fast response NH_3 sensor of the $MAPbI_3$ film. It is worth noting that this sensor is based on the change of electrical property, which is of more practical significance than that based on the change of optical property, because electrical property is much easier to be detected then optical property.

The above proposed processes occurring when the $MAPbI_3$ film exposed in NH_3 was also reflected in the color change of the film induced by NH_3. Previous work showed that the color of the $MAPbI_3/TiO_2$ film changed reversibly when exposed to NH_3, and the reversibility was destroyed when the exposure time increased to tens of minutes.[19] We found that, for the NH_3 induced color change of the pure $MAPbI_3$ films, the reversibility was completely destroyed in a shorter exposure time (<50 s). Fig. 2 shows the optical characterizations of the pristine perovskite $MAPbI_3$ film and the recovered film after exposed in NH_3 for 5 s and 50 s. The right frame shows the digital photographs, the left frame shows the transmittance spectra. The pristine perovskite $MAPbI_3$ film displays brown color. The transmittance spectrum tells that the perovskite $MAPbI_3$ film keeps low transmittance below 755 nm, and increases sharply at 755 nm, which agree with the band gap of perovskite $MAPbI_3$. When exposed in NH_3 atmosphere for about 5 s, the color of the film could not be completely restored to the original brown but changed to light brown after the NH_3 atmosphere was removed. It can be seen that, compared to that of the pristine perovskite $MAPbI_3$ film, the transmittance of the film after exposed in NH_3 for 5 s increased across the entire visible region. In addition to 755 nm, an absorption edge at around 500 nm appeared, indicating that a new phase appeared after the film was exposed in NH_3 for 5 s. When exposed in NH_3 for a longer period of time (about 50 s)

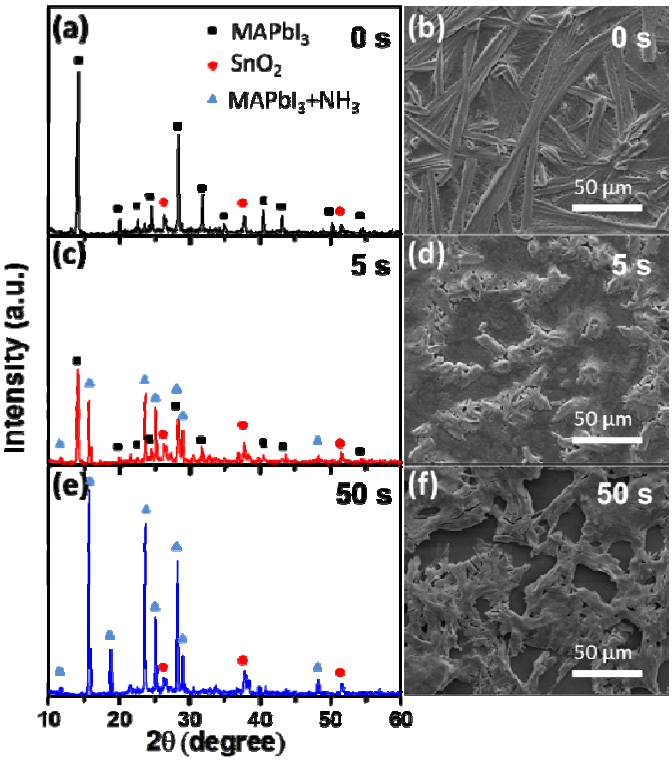

Fig. 3 XRD patterns (a, c, e) and SEM images (b, d, f) of the perovskite $MAPbI_3$ film before (a, b) and after exposed in the NH_3 atmosphere for 5 s (c, d) and 50 s (e, f).

the film kept light yellow color after the NH_3 atmosphere was removed. The film showed single absorption edge at around 500 nm and homogeneous high transmittance at the longer wavelength region, suggesting that the perovskite $MAPbI_3$ has been transformed into the new phase absolutely. Though the color change in one sample caused by the irreversible reaction of perovskite $MAPbI_3$ and NH_3 is unrepeatable, the resistance change is repeatable because the new product generated from the irreversible reaction also shows similar NH_3 induced resistance change character to perovskite $MAPbI_3$. Therefore, this electrical-based NH_3 sensor shows better repeatability and stability compared to optical-based one.

To further understand the phase transformation and the morphology change induced by NH_3 on the perovskite $MAPbI_3$ film, we carried out X-ray diffraction (XRD) measurements and morphology characterizations on the pristine perovskite $MAPbI_3$ film and that after exposed in the NH_3 atmosphere for different period of time. The results were exhibited in Fig. 3. The XRD pattern and scanning electron microscopy (SEM) image of the pristine perovskite film were shown in Fig. 3(a) and (b). The XRD pattern indicates that $MAPbI_3$ has a tetragonal perovskite structure (peaks marked with squares). The diffraction peaks at about 14.02 19.94, 28.42, 31.78, 40.48 and 43.04 degree correspond to the reflections from (110), (112), (220), (310), (224) and (314) crystal planes respectively. No PbI_2 and other impurity peaks other than the ones attributed to FTO (marked with circles) are observed. SEM image in Fig. 3(b) shows that the pristine perovskite $MAPbI_3$ film is rough and continuous, which shows the same morphology as previously reported.[20] After exposed in the NH_3 atmosphere, a new phase appears in the perovskite $MAPbI_3$ film. The XRD pattern in Fig. 3(c) shows that, after exposed in NH_3 for 5 s, intensities of all the diffraction peaks belonging to tetragonal perovskite structure are reduced and new diffraction peaks (marked with triangles) belonging to a new phase ($MAPbI_3$+NH_3) appears. Meanwhile, the morphology of the film was reconstructed and the coverage and smoothness were increased (Fig. 3(d)), which was similar to the phenomenon when fumigated in DMF vapor as we reported previously.[23] The reconstruction of the film may results from the difference of the crystal structure before and after the reaction with NH_3. After exposed in NH_3 for a longer period of time (about 50 s), the film transformed into the new phase completely (Fig. 3(e)). And the morphology of the film changed obviously: the roughness increased and the coverage decreased greatly (Fig. 3(f)). The discontinuous of the film may be an important reason of the greater resistance of the $MAPbI_3$+NH_3 film compared to the pristine perovskite $MAPbI_3$ film.

In addition to NH_3, we have also studied the resistance change of perovskite $MAPbI_3$ film induced by moisture. Fig. S3 (ESI†) shows the I-V curves and I-t curve of the perovskite $MAPbI_3$ film in dry N_2 and air with a relative humidity (RH) of about 50% at RT. The results indicate that a similar resistance change effect also can be induced by moisture in perovskite $MAPbI_3$.

In conclusion, we have investigated the resistance change of the perovskite $MAPbI_3$ film induced by NH_3. It was found that when the perovskite $MAPbI_3$ film was exposed to NH_3 the current through the film was greatly improved within seconds. When the NH_3 environment was removed, the current was decreased to the original value within seconds. XRD pattern and SEM images showed that when exposed in NH_3 perovskite $MAPbI_3$ gradually transformed to a new phase and the morphology of the film changed significantly. The resistance of this new material was sensitive to NH_3 as that of perovskite $MAPbI_3$. The results of this study imply that $MAPbI_3$ could potentially be used as room-temperature-working NH_3 sensor with fast response time. Meanwhile, understanding how perovskites $MAPbI_3$ interact with the surrounding environment is of great significance to improve the stability of the perovskite solar cells.

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