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Chemoresistive Humidity, NO_2 and H_2 Sensor Based on 2D-$CrCl_3$ Layered Trihalides Nanoflakes

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Summary:

Herein we demonstrate that few-layers 2D-$CrCl_3$ transition metal trihalides (TMTHs) MX_3 (M= Ti, V, Cr, Mo, Fe, Ru and X = Cl, Br, I), exhibit unveiled capabilities as chemoresistive *p*-type sensors to humidity (10 - 80% RH @25 °C), NO_2 (400 ppb – 1 ppm) and H_2 (10 – 250 ppm) at 100 °C operating temperature (OT). Specifically, we investigated the humidity response mechanism unraveling the nature of the reversal of the resistance from an ionic (@25 °C OT) to an electronic conduction regime (@100 °C OT) in humid air conditions. All these findings suggest 2D-$CrCl_3$ platforms as 2D novel interfaces for humidity and gas sensing applications.

Keywords: 2D-$CrCl_3$, chemoresistive, humidity sensor, NO_2, H_2 gas sensor.

Background, Motivation an Objective

There are substantial efforts to replace traditional metal oxides (MOX) gas sensors with 2D van der Waals (vdW) materials, which offer the advantage of having the maximum surface-volume ratio as respect to their MOX counterparts [1]. Excluding the applications of Transition Metal Trihalides (TMTHs), with formula MX_3 (M = Ti, V, Cr, Mo, Fe, Ru and X = Cl, Br, I), as cleavable 2D ferromagnetic semiconductors, the humidity and gas sensing response of few layers MX_3 TMTHs are still unknown, probably on the assumption that their environmental instability in dry/wet air prevents their utilization as reproducible gas sensor interfaces. Within the family of TMTHs, we found that $CrCl_3$ is the only relative stable under ambient laboratory conditions even after its isolation in reduced dimensionality through mechanical exfoliation. Specifically, we revealed that $CrCl_3$ has O-$CrCl_3$ stable semi-oxidized surface phase which is stable up to 400 °C with charge imbalance [2]. We therefore concluded that, from the operational point of view, few-layers 2D-$CrCl_3$ do not suffer dramatic oxidation or evaporation phenomena up to 200 °C, suggesting $CrCl_3$ to be a potential chemoresistive platform, operating in the 25 – 150 °C temperature range and dry/wet environmental conditions, for gas sensing applications.

Description of the New Method or System

In this study, commercial powders of $CrCl_3$ have been for the first time exfoliated by Liquid Phase Exfoliation (LPE) to produce reproducible amounts of few-layers 2D-$CrCl_3$, having a thickness of 20 - 25 nm and aspect ratio of ~205 [3]. Well dispersed exfoliated flakes were successfully deposited by spin coating over interdigitated Pt patterned electrodes to yield thin film, as shown in Fig. 1.

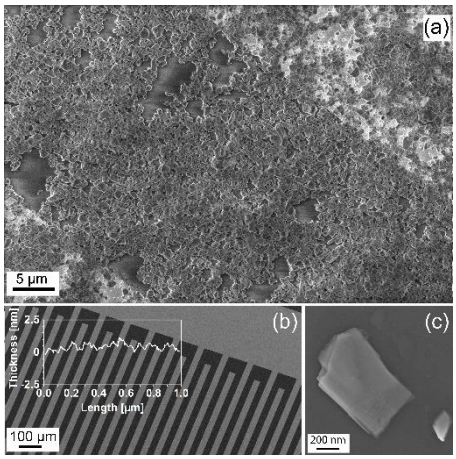

Fig. 1. (a) exfoliated $CrCl_3$ flakes deposited on Si_3N_4 substrate with Pt-interdigital electrodes (lighter regions) (b), comb-like picture of the Pt electrodes with roughness profile (inset) of the Si_3N_4 substrate. (c) SEM magnification of a representative $CrCl_3$ flake after exfoliation.

Results and Discussion

We firstly investigated the electrical response to humidity ((10 – 80% @25 °C) increasing the operating temperature (OTs) from 25 °C to 150 °C as shown in Fig. 2.

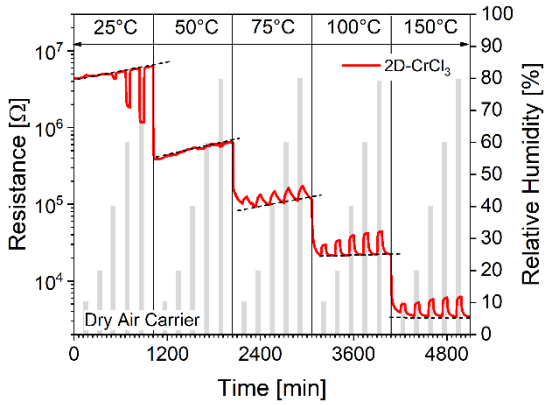

Fig. 2. Humidity response of exfoliated 2D-$CrCl_3$ in the 10 - 80% RH range (RH @25 °C) and different operating temperatures from 25 to 150 °C.

At 25 °C with increasing humidity from 10 - 80% RH, resistance decreases whereas at OTs > 75 °C resistance increases with increasing humidity. Remarkably, with increasing OTs, the experimental limit of detection (LOD) improves. At 25 °C LOD is ~ 40% RH while at OTs > 75 °C, LOD is as small as ~ 10% RH. Furthermore, with increasing the OTs, the drift of the base line resistance, related to incomplete desorption of water molecules, is fully compensated (compare the slopes of the black dotted lines) indicating 100 °C as the best operating temperature for humidity detection in the whole 10 - 80% RH range. Interestingly, 50 °C OT represents a transition zone between the reversal response (i.e. decrease/increase) of the electrical resistance, on the assumption of a different reaction mechanism (i.e., ionic/electronic).

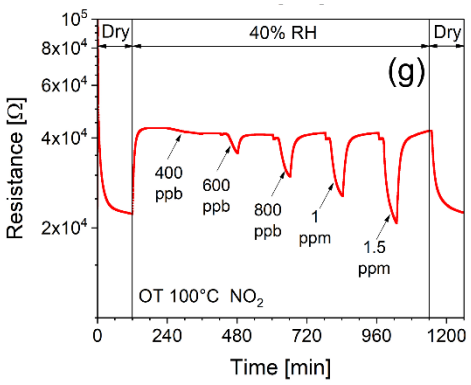

Fig. 3. Electrical response in 40% RH humid air background to NO_2 (400 ppb - 1.5 ppm) and 100 °C OT.

Exposing the sensor to NO_2, it shows that 2D-$CrCl_3$ behaves as a *p*-type interface with decreasing/increasing sensor's resistance to NO_2 (oxidizing) and H_2, gases respectively (here not shown), in the whole OTs range. In the OTs range 100 – 150 °C sensor's electrical response is fully developed with appreciable changes of the electrical signal and good recovery of the base line after gas desorption, suggesting 100 °C as the best operating temperature for investigated gases detection.

Two humidity sensing mechanism have been proposed considering a low (25 °C) and high (100 °C) temperature working regime (Fig. 4). At 25 °C, H_2O dissociatively chemisorbs over 2D-$CrCl_3$, leading to the formation of two hydroxyls (OH). With increasing the humidity content, further H_2O physisorbed layers are formed, enabling, at higher RH%, the onset of a Grotthus proton-chain (H^+) ionic-conduction mechanism (Fig. 4b). At T > 100 °C, the physiosorbed water is almost desorbed and a direct electronic charge interaction mechanism takes place between the $CrCl_3$ surface and the adsorbing H_2O/gases. In this case the response mechanism is fully electronic (Fig. 4c).

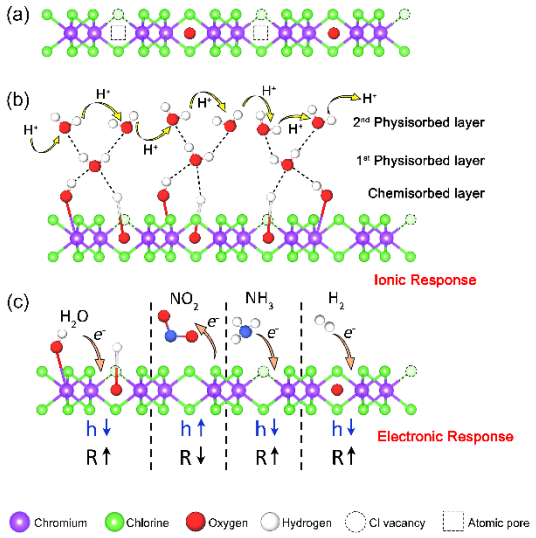

Fig. 4. (a) side view of a mono layer $CrCl_3$ structure showing a tri-layer atomic assembly (Cl-Cr-Cl); (b) schematic model of humidity adsorption at 25 °C and ionic (H^+) conduction mechanism; (c) schematic model of H_2O, NO_2, NH_3 and H_2 gases interaction (indicated the charge transfer from/to the adsorbing molecules and the surface).

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