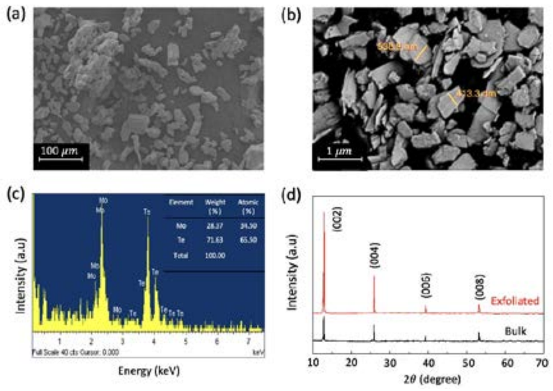
Significant Enhancement of the NO_2 Detection Response in $MoTe_2$ Nanostructure with a 1T′-2H Structure Mixture

Shiu-Ming Huang,[1,2] Wei-Chueh Cheng,[1] Pin-Cing Wang,[1] Fu-En Cheng,[1] and Chiu-Hsien Wu[3,4]
1. Department of Physics, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
2 Center of Crystal Research, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
3 . Department of Physics, National Chung Hsing University, Taichung 402, Taiwan
4. Institute of Nanoscience, National Chung Hsing University, Taichung 402, Taiwan

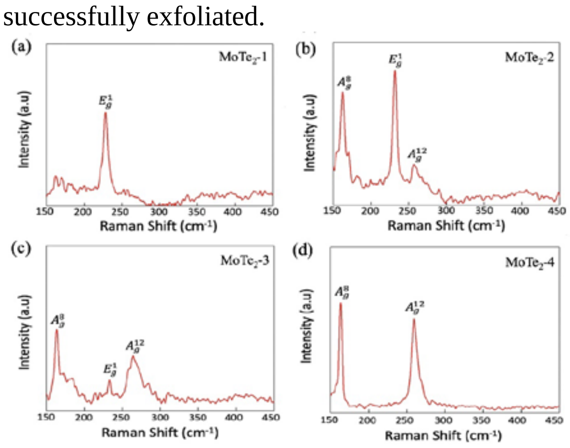
Abstract
- The NO_2 detection is investigated in the liquid phase exfoliated $MoTe_2$ nanoparticle cluster.
- The detection response was enhanced by 2 orders through appropriate 2H and 1T′ structural mixture achieved through thermal annealing processes.
- The observed responses reached 38% at 25 ppb and 120% at 500 ppb, and the limit of detection is 2.73 ppb.
- This enhancement originates from reducing effective contact resistance from the metallic 1T′ structure, and carrier contribution from the semiconducting 2H structure.

Experiment method
- $MoTe_2$ micro-particle was exfoliated to $MoTe_2$ nano-particle through the liquid phase exfoliateion method.
- The exfoliated $MoTe_2$ nano-particles partially tranform from 2H structure to 1T′ strcutre through thermal annealing processes.
- Four $MoTe_2$ nano-particles devices were prepared at different temperatures and periods, and they contain different nanostructure ratio of 2H to 1T′.
- These $MoTe_2$ nano-particles were dropped on the pre-patterned Au electrode stbstrate for NO_2 detection.

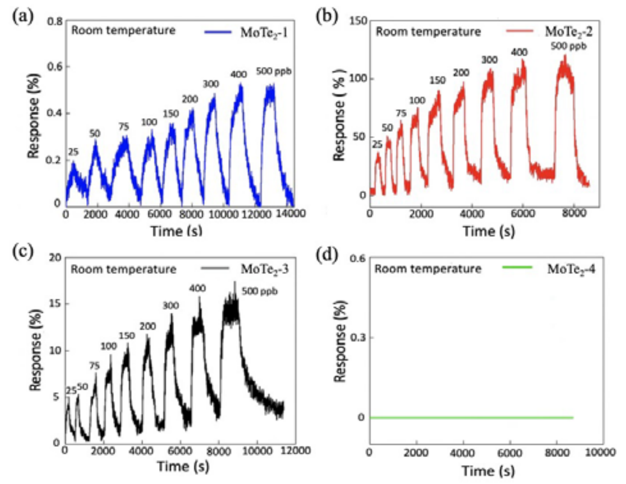
Results and Discussions



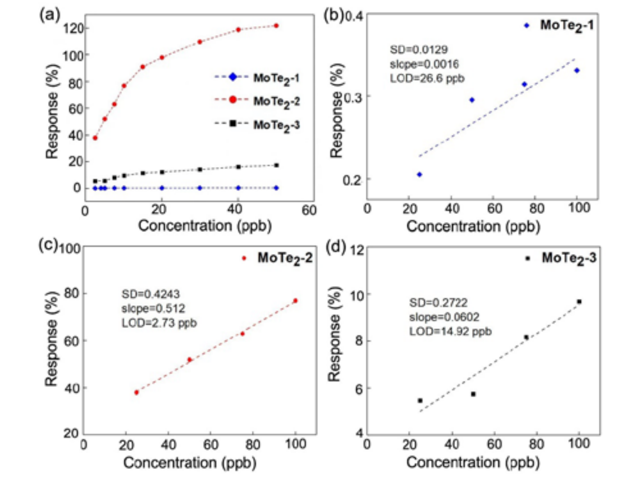
- The SEM image show that the exfoliated $MoTe_2$ particle size is roughly reduced by 2 orders.
- The energy-dispersive X-ray spectroscopy (EDS) analysis. The peaks correspond to the element of Mo and Te and the result reveals the ratio of Mo : Te = 1 : 1.9.
- For the (002) peak, the intensity of the peak is observed to be significant higher after exfoliation process, indicating that MoTe2 under that plane was successfully exfoliated.



- $MoTe_2$-1: without thermal annealing.
  $MoTe_2$-2 and $MoTe_2$-3: thermal annealing at 250 ◦C for 30 minutes.
  $MoTe_2$-4: thermal annealing at 300 ◦ C for 30 minutes.
- The E^1_g is the oscillation mode of 2H structure (semiconductor).
  A^8_g and A^{12}_g are the oscillation modes of 1T′ structure (metal).
- $MoTe_2$-1 only exhibits E^1_g peak and that indicates there is only 2H structure in pristine $MoTe_2$ particles.
- $MoTe_2$-2 and $MoTe_2$-3 show A^8_g, A^{12}_g and E^1_g peaks.
  This indicates that partial $MoTe_2$ particles transfer from 2H structure to 1T′ structure after thermal annealing at 250 ◦C for 30 min.
- $MoTe_2$-4 shows the A^8_g and A^{12}_g peaks, and no E^1_g peaks are detected. This indicates that $MoTe_2$ particles completely transfer from 2H structure to 1T′ structure, and no 2H structure are detected after thermal annealing at 300 ◦C for 30 min.
- 2H is a weak stable structure and would transfer to the 1T′ structure through external thermal annealing. These reveal that one could tune the $MoTe_2$ structure component through thermal annealing processes.



- The detection response increases with NO_2 concentration increase.
  This can be explained by the fundamental principle of NO_2 gas sensing in semiconductor $MoTe_2$ through the charge-transfer processes between NO_2 and $MoTe_2$.
- $MoTe_2$-4 exhibits no response in our experimental NO_2 concentration range.
- 2H semiconductor structure exists in the $MoTe_2$-1, $MoTe_2$-2 and $MoTe_2$-3 while no 2H semiconductor structure is found in the $MoTe_2$-4.
  This result supports that the hole carrier contribution from the semiconductor structure is a critical mechanism for NO_2 detection in the $MoTe_2$.

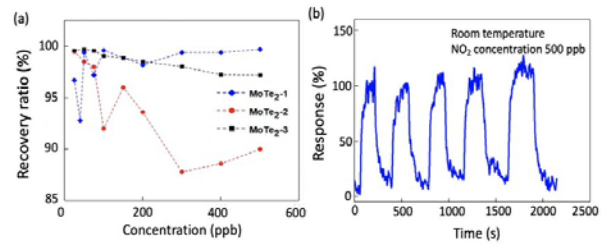


Device	25 ppb	500 ppb	Limit of Detection (Structure)
MoTe2-1	0.2 %	0.5 %	26.6 ppb (2H)
MoTe2-2	38 %	120 %	2.73 ppb (2H+1T’)
MoTe2-3	5 %	18 %	4.92 ppb (2H+1T’)
MoTe2-4	0 %	0 %	No Data (1T’)

- The response improves in devices with the thermal annealing that makes samples composed of 2H and 1T′ structure.
- The 1T′ structure is a metal that could reduce effective contact barrier height in the whole system.
- This result reveals that it is possible to greatly enhance the NO_2 detection response by appropriately tuning the 2H and 1T′ components of $MoTe_2$ via thermal annealing.

The reported NO_2 detection response in various types of 2D TMDs at low NO_2 concentraton.

Material	NO_2 (ppb)	Response (%)
WS_2	50	5.06
WS_2	100	9.3
WSe_2	50	15
MoS_2	100	50
MoS_2	20	25
MoS_2	20	20
$MoTe_2$	100	140
$MoTe_2$	20	18
$MoTe_2$	1000	1300
$MoTe_2$ (This work)	25	38
$MoTe_2$ (This work)	500	120



- (a) shows the recovery ratio as a function of the NO_2 concentration. The recovery ratio is higher than 85% for the NO_2 gas concentration that ranged from 25 to 500 ppb. This recovery ratio is much higher than all reported values in the 2DTMDs systems with and without external artificial treatments.
- (b) shows five consecutive detecting cycles, demonstrating the capability of continuous sensing, reversibility, and stability.

Conclusions
- NO_2 detection was investigated in the $MoTe_2$ nanostructure at room temperature. The detection responses were 0.2% at 25 ppb and 0.5% at 500 ppb in the 2H structure, while no detection response was measured from 25 to 500 ppb in the 1T′ structure.
- The detection response was enhanced by two orders in $MoTe_2$, with a mixture of a 2H and 1T′ structure achieved via thermal annealing. The detection response reaches 38% at 25 ppb and 120% at 500 ppb.
- This great enhancement originates from reducing the effective contact resistance from metallic 1T′ structure.
- The limits of detection of the samples $MoTe_2$-1, $MoTe_2$-2, and $MoTe_2$-3 are 26.6, 2.73, and 4.92 ppb, respectively.
- The high recovery ratio, reversibility, stability, and the low level concentration detection (25 ppb) make the MoTe2 with tunable 1T′-2H structure mixture more reliable for potential applications.