DOI 10.5162/IMCS2018/GS2.4

UV light enhanced room temperature NO_2 gas sensors based on Au loaded organic–inorganic hybrid perovskite incorporated with tin dioxide

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Abstract :
A novel NO_2 sensing material Au/$MASnI_3$/ SnO_2 was fabricated by coupling a light-sensitive material, Au decorated organic-inorganic hybrid perovskite (Au/$MASnI_3$), with a wide band gap gas sensing semiconductor materials, tin dioxide (SnO_2), via a simple calcination process. The physical and gas sensing properties of these prepared Au/$MASnI_3$/SnO_2 composite toward NO_2 gas at room temperature in dark and under 365 nm UV illumination were examined. The characterization demonstrates the formation of a p-n heterojunction structure between p-$MASnI_3$ and n-SnO_2. Due to to the good synergistic effect of the ternary materials, including the high light absorption of $MASnI_3$, the surface plasmon resonance and the active catalytic effect of Au nanoparticles and the special interactions at $MASnI_3$/SnO_2 heterojunction, the Au/$MASnI_3$/SnO_2 sensor obtained by calcining Au/$MASnI_3$ at 230°C (named as MSA230) exhibits superior gas sensing performance toward NO_2 with high sensitivity (Rg/Ra= 240 up to 5 ppm NO_2), ultra-fast recovery time (about 12s) and excellent selectivity as compared to the SnO_2 and SnO_2/Au counterparts at room temperature under UV illumination. All these characters make it more possible to be used as sensor material widely.

Key words: gas sensing, NO_2, $CH_3NH_3SnI_3$, room temperature, UV

Results and Discussion

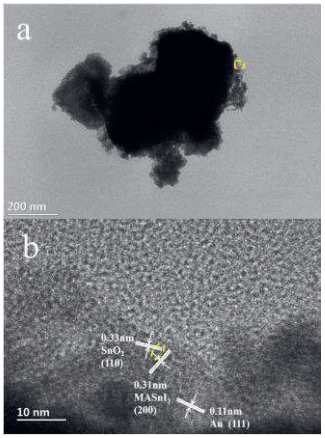

Fig.1 (a-b) HRTEM image of MSA230 composite.

Fig.1 depicts the HRTEM images of MSA230 with different magnifications. The lattice fringes in Fig.1b was measured to be 0.33, 0.31 and 0.11 nm, which can be assigned to SnO_2, $MASnI_3$ and Au, respectively. It can be deduced that the Au/$MASnI_3$/SnO_2 was successfully fabricated and p-n heterojunctions between $MASnI_3$ and SnO_2 were formed in composite, which is in accord with the I-V measurement results.

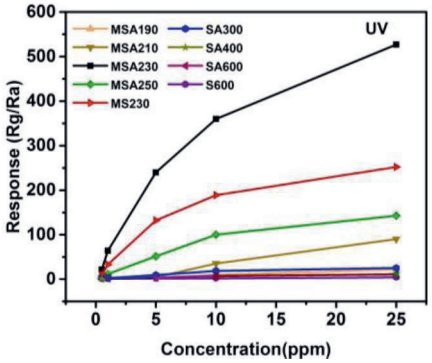

Fig.2 The corresponding response of the as-prepared samples are plotted against NO_2 concentration at room temperature with UV illumination.

As shown in Fig.2, the response of the sensor using MSA230 to 5 ppm NO_2 increased from 17.2 in dark to 240.6 under UV light illumination. This illustrates that UV illumination increases the carrier density and reduces the depletion layer width, making it possible to provide more

electrons for the oxidizing gas, therefore, the sensors show high responses to NO_2. Comparing to the MSA230 sensor, the responses of the others were not enhanced as dramatically as the sensor based on the MSA230. This is because that a high content of $MASnI_3$ would reduce the contact between the target gas and SnO_2 and a high content of SnO_2 also would decrease the density of the photogenerated carriers excited by $MASnI_3$.

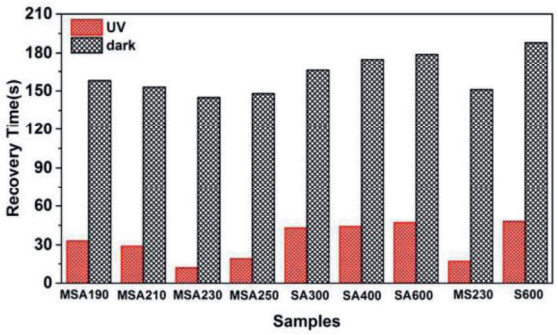

Fig.3 Recovery time of the sensor based on various samples towards 5 ppm NO_2 with and without UV light illumination at room temperature.

As shown in Fig.3, with and without UV light illumination, the recovery time of the sensor using MSA230 is 12s and 154s, respectively. With UV light illumination, the photogenerated electron improved the surface oxidation activity and accelerated the surface reaction and the photogenerated holes can also reacted with NO_2, leading to a much faster recovery time.

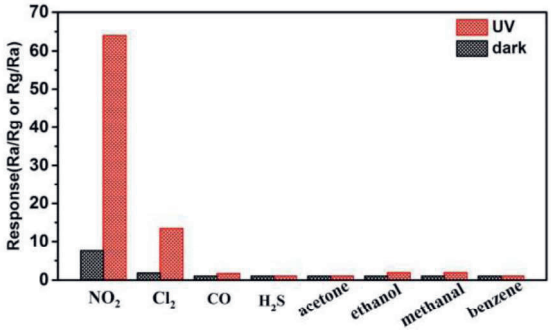

Fig.4 Selectivity of the sensor based on the MSA230 towards different gases in dark and with UV light illumination at room temperature.

Fig.4 illustrates the selectivity of the sensors to 5 ppm NO_2, 10 ppm Cl_2, 50 ppm CO, H_2S, acetone, ethanol, methanal and benzene at room temperature with and without UV light illumination. Among these target gases, the MSA230 sensor demonstrated a dramatically higher response to NO_2 than the other gases with UV light stimulation, proving that the p–n heterojunction nanostructure of the sensor based on MSA230 has a high response and selectivity to NO_2 gas at room temperature under UV light illumination.

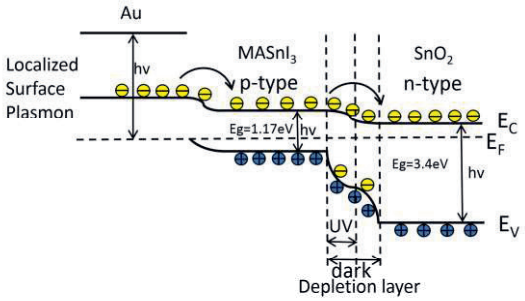

Fig.5 Energy band diagram of $Au/MASnI_3/SnO_2$ system after equilibrium at room temperature under UV illumination.

In the case of $Au/MASnI_3/SnO_2$ (Fig.5.), Due to the formation of favorable n–p heterojunction in between p-type $MASnI_3$ and n-type SnO_2, upon UV light irradiation electrons will migrate from CB of $MASnI_3$ to the CB of SnO_2, leaving behind a hole in the VB of $MASnI_3$, which can effectively inhibit the charge recombination process. Meanwhile, because of SPR excitation, photoexcited state of Au is higher than the CB of $MASnI_3$ and produces hot electrons. First electron will migrate to the CB of $MASnI_3$ and then to avoid the charge recombination, electron will quickly move to the CB of SnO_2. The presence of huge number of electrons in the CB of SnO_2 facilitates the gas sensing efficiency of $Au/MASnI_3/SnO_2$ nanocomposites.

In conclusion, that the $Au\text{-}MASnI_3/SnO_2$ sensor possesses outstanding gas sensing property toward NO_2 at room temperature with UV light stimulation can be attributed to the good synergistic effect of the ternary materials, including the high light absorption of MASnI3, the surface plasmon resonance and the active catalytic effect of Au nanoparticles, and the p-n heterojunction between $p\text{-}MASnI_3$ and $n\text{-}SnO_2$.

The authors thank the supports of National Natural Science Foundation of China (no.61671284 and U1704255).

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