DOI 10.5162/IMCS2018/P2GS.4

WS_2-decorated rGO for Quasi-room Temperature Gas Sensing Applications

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Abstract:

We report on the NO_2 and humidity chemoresistive gas responses of reduced graphene oxide (rGO) and WS_2-decorated rGO (GO/WS_2). Films are prepared by drop casting a solution of GO and WS_2 suspended nanoflakes in ethanol, on Si_3N_4 patterned substrates to yield a homogeneous dispersion of WS_2 on the GO matrix as shown by HRTEM microstructural characterization. After thermal reduction at 70°C, rGO and rGO/WS_2 gas sensing response are compared, exposing the films to NO_2 (2-10 ppm) in dry air and 60% Relative Humidity (R.H.) at quasi room temperature (i.e. 25°C and 50°C). WS_2 addition improves the stability of the baseline, and poses improved sensitivity to NO_2. Finally, the effect of visible light illumination on gas desorption mechanism is examined, observing a positive effect on the base line recovery after gas evacuation.

Key words: WS_2, rGO, NO_2, humidity, light

It is well known that rGO and WS_2 layered nanoflakes respond to oxidizing and reducing gases as previously resported. [1,2] This paper reports on WS_2-decorated rGO prepared by mixing a certain amount of exfoliated WS_2 flakes, obtained by ball milling assisted sonication, dispersed in ethanol with a solution of graphene oxide prepared by Hummer's method, followed by a short sonication to homogenize the dispersion and avoid agglomeration. Obtaining GO/WS_2 system is confirmed by the microstructural analysis carried out by TEM characterization shown in Figure 1. The black "islands" are WS_2 flakes, while the substrate is made of a thin, continuous and uniform layer of GO. Statistical analysis of the TEM image revealed that in an area of almost 80 μm^2, the whole surface is covered by the GO sheets as the folded edges of GO sheets are clearly visible, while more than 6% of this surface is covered by WS_2 flakes, with average particle size of ≈100 nm.

Considering the importance of the extent of GO reduction and its effects on the stability of the baseline [3], in this work the degree of reduction of GO has been controlled by maintaining the annealing temperature below 100°C. To this extend, thermal reduction has been carried out at 70°C for 30 min and the operating temperature for gas sensing is maintained below this value to preserve the material's characteristics. The electrical resistance of GO and GO/WS_2 films in air (R_{air}) as a function of temperature is presented in figure 2a. As seen, the semiconducting behavior of the films, as well as the equilibrium state and recovery of the electrical response are remarkably improved by WS_2 decoration of GO sheets. As the fastest response is obtained at 50°C, this temperature is considered as the operating temperature of the electrical sensing measurements.

The sensitivity of the films to different concentrations of NO_2 at room and near room temperature is presented in Figure2b. 2ppm NO_2 is detected even at room temperature but, as expected, with a very poor recovery of the base line. On the other hand, 2 ppm NO_2 is well detected at 50°C with a faster recovery. The evidence coming from the comparison of the two sensors is that, given the same amount of GO, the presence of WS_2 is fundamental to have a reasonable response as NO_2 gas sensor.

Figure 2c shows the NO_2 sensing in presence of humidity (cross sensitivity test). As expected, water vapor acts like a reducing agent and the base-line resistance increases when exposed to humidity, indicating charge transfer from water molecules to the surface.

Cross sensitivity to humidity is reduced at 50°C operating temperature, as shown by comparing panel (b) and (e) of figure 2c.

In the case of room temperature sensing, the presence of humidity improves the relative response as respect to the 50°C operating temperature, although the baseline is not recovered after desorption (panel b). Figure 2d depicts the sensor's performance when illuminated by blue light (λ=430nm). Light illumination of semiconductor gas sensors has shown promising results in terms of recovery of the base line, [4] and it is confirmed for rGO/WS_2 heterostructure. As seen in figure 2d, light illumination does not change the base line, but promotes gas desorption and fully recovers the base line, either at 25°C or 50°C.

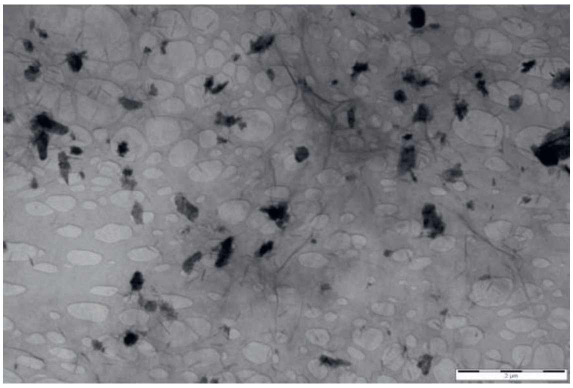

Fig. 1. Low resolution TEM image of 80 µL Low resolution TEM image of 80 µL of the WS_2-decorated GO solution deposited on a lacey grid. Scale bar is 2µm.

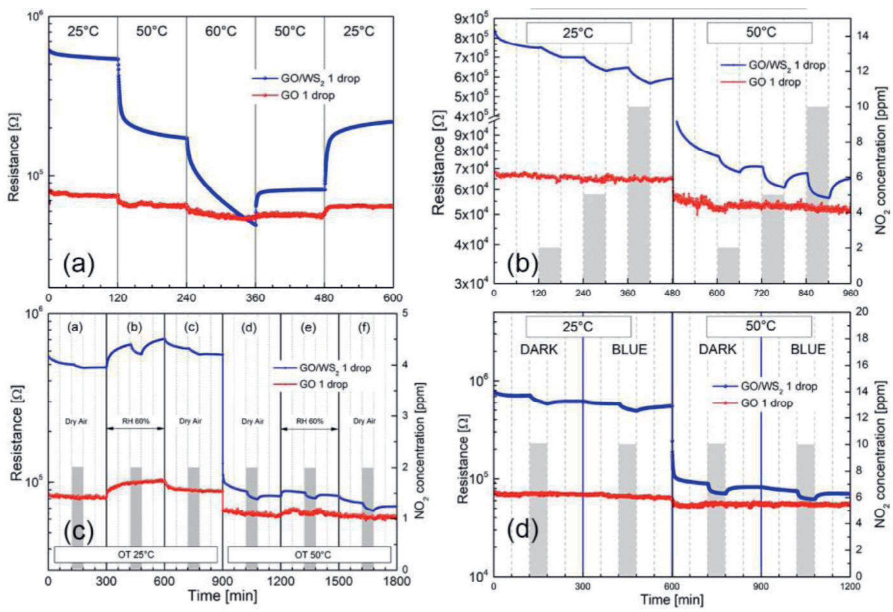

Fig.2.(a) Base line at different temperatures after GO reduction, (b) sensitivity to NO_2 at 25°C and 50°C operating temperature, (c) cross sensitivity to 60%RH and NO_2 at 25°C and 50°C operating temperature, (d) Influence of light on sensitivity to NO_2 at 25°C and 50°C operating temperature

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