

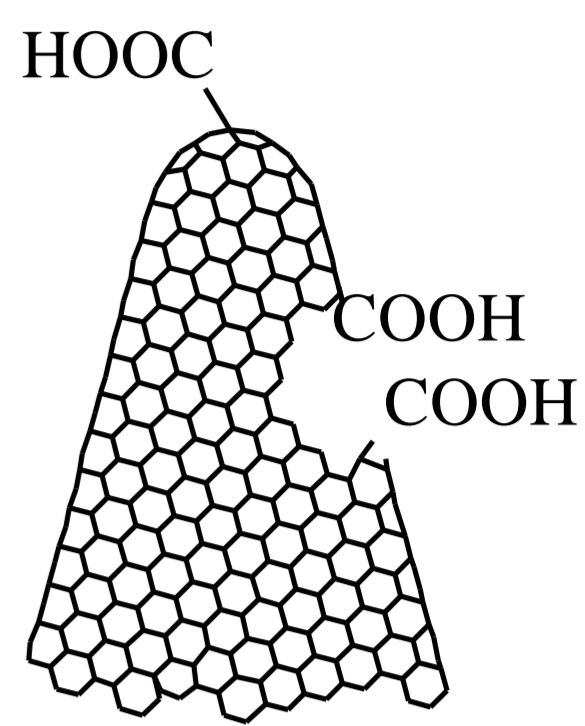
QUATERNARY OXIDIZED CARBON NANOHORNS - BASED  
NANOHYBRID FOR RESISTIVE HUMIDITY SENSOR  
EUROPEAN GRANTED PATENT EP3992623B1, 07/05/2023  
ASSIGNEE: National Institute for Research and Development in  
Microtechnologies - IMT Bucharest



Inventors: BOGDAN- CATALIN SERBAN, OCTAVIAN BUIU, CORNEL COBIANU, VIOREL AVRAMESCU, NICULAE DUMBRAVESCU

## INTRODUCTION

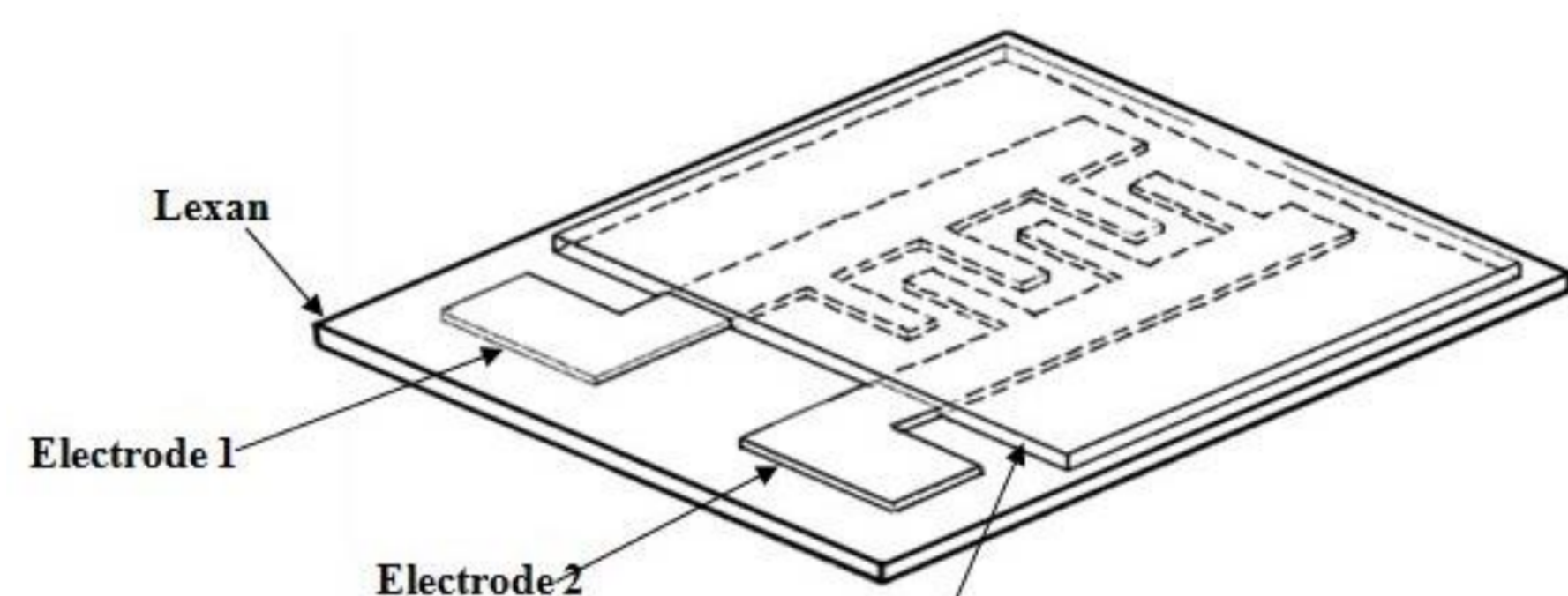
- The present invention relates to the RH sensing response of a resistive sensor employing a sensing layer based on quaternary nanohybrid composition comprising or consisting of  $CNH_{OX}/SnO_2/ZnO/PVP$  at 1.5/1/1/1 w/w ratio to 3/1/1/1 w/w ratio. When employed as RH sensing layers, these quaternary nanohybrid compositions exhibit several significant advantages:
- Oxidized carbon nanohorns ( $CNH_{OX}$ ) (**FIG 1**) have high specific surface area/volume ratio, water molecules affinity and show rapid electrical resistance variation when RH varies from 0% to 90%.
- The nanometric tin (IV) oxide ( $SnO_2$ ) nanopowder exhibits good RH sensitivity.  $CNH_{OX}$  have p-type electrical conduction (through holes), while  $SnO_2$  is a n-type metallic oxide semiconductor (through electrons). By adding  $SnO_2$  to  $CNH_{OX}$ , one will obtain islands of p-n semiconductor heterojunctions embedded in PVP (a dielectric material) that increase the sensitivity of the sensitive layer.
- Zinc oxide ( $ZnO$ ) nanopowder exhibits good RH sensitivity. Both  $ZnO$  and  $SnO_2$  are n-type electrical conductors. The  $ZnO - SnO_2$  nanocomposite has sensing properties superior to each of the single oxides, because each of the oxides interacts differently with the oxidized carbon nanohorn material, leading to alterations in the pore distribution, which increase the specific surface area;
- Polyvinylpyrrolidone (PVP) is a hydrophilic polymer with excellent binding properties, which enables its employment in sensing structures with either flexible or rigid substrate;
- Detection at room temperature, low response time, low cost, small size, simplicity in manufacture.



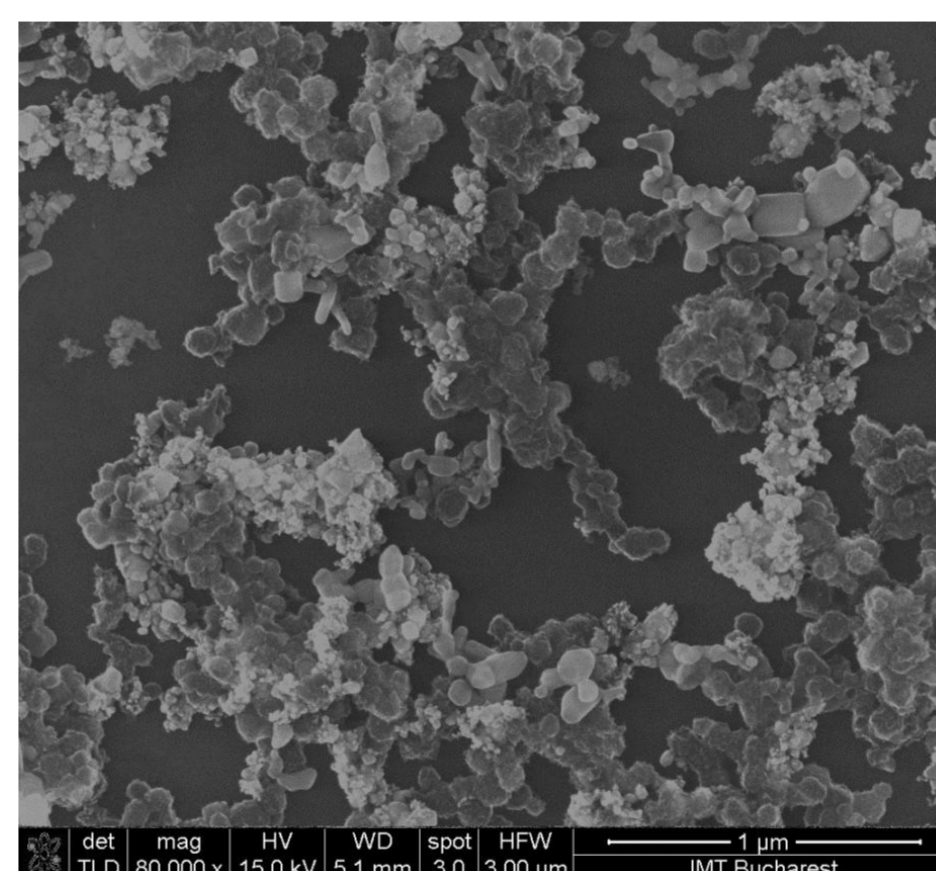
**FIG 1 –**  
Structure of  
oxidized carbon  
nanohorns  
( $CNH_{OX}$ )

## MATERIALS, METHODS, RESULTS

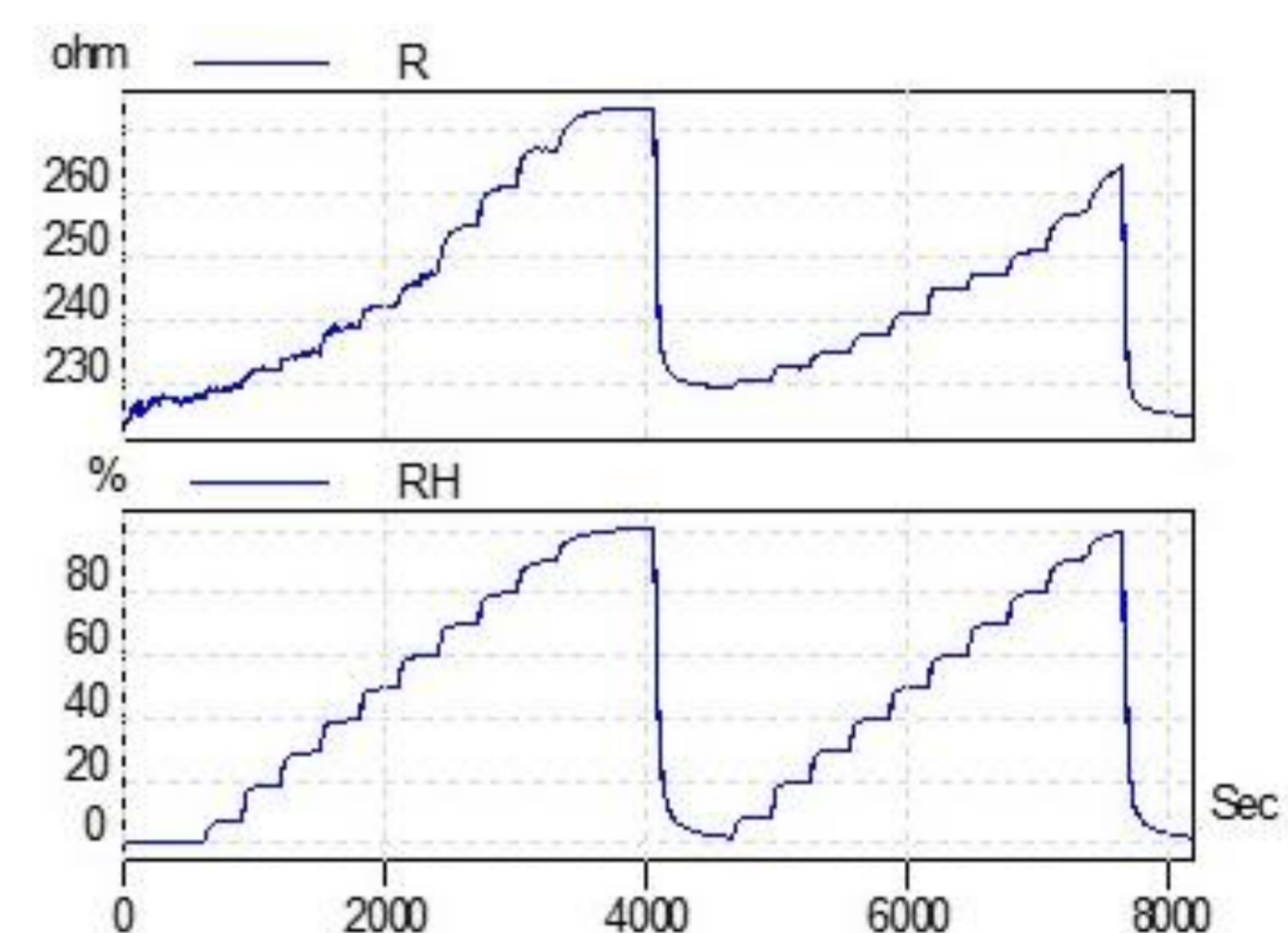
- The interdigitated (IDT) sensing structure (**FIG 2**) can be manufactured on Lexan, Kapton, or glass. The dielectric substrate may have a thickness from 5 to 50  $\mu m$ . The electrodes can be made from the same material or can be formed of different materials. The electrodes can be made from conductive materials such as gold and chromium. A dispersion formed in isopropyl alcohol of a nanohybrid sensing layer described above, at different w/w ratios, was deposited on the IDT structure using the drop casting method (**FIG 3**).
- The RH sensing capability of the proposed sensitive layers was investigated by applying a current between the two electrodes and measuring the voltage at different RH values.
- Measurements were performed in humid nitrogen at RT and compared with the response of a commercial capacitive RH humidity sensor, provided with signal-processing and signal-amplifying electronics (**FIG 4** and **FIG 5**). From the detection principle point of view, the resistance of the sensitive layer varies with the RH level.



**FIG 2 –** IDT  
sensing  
structure

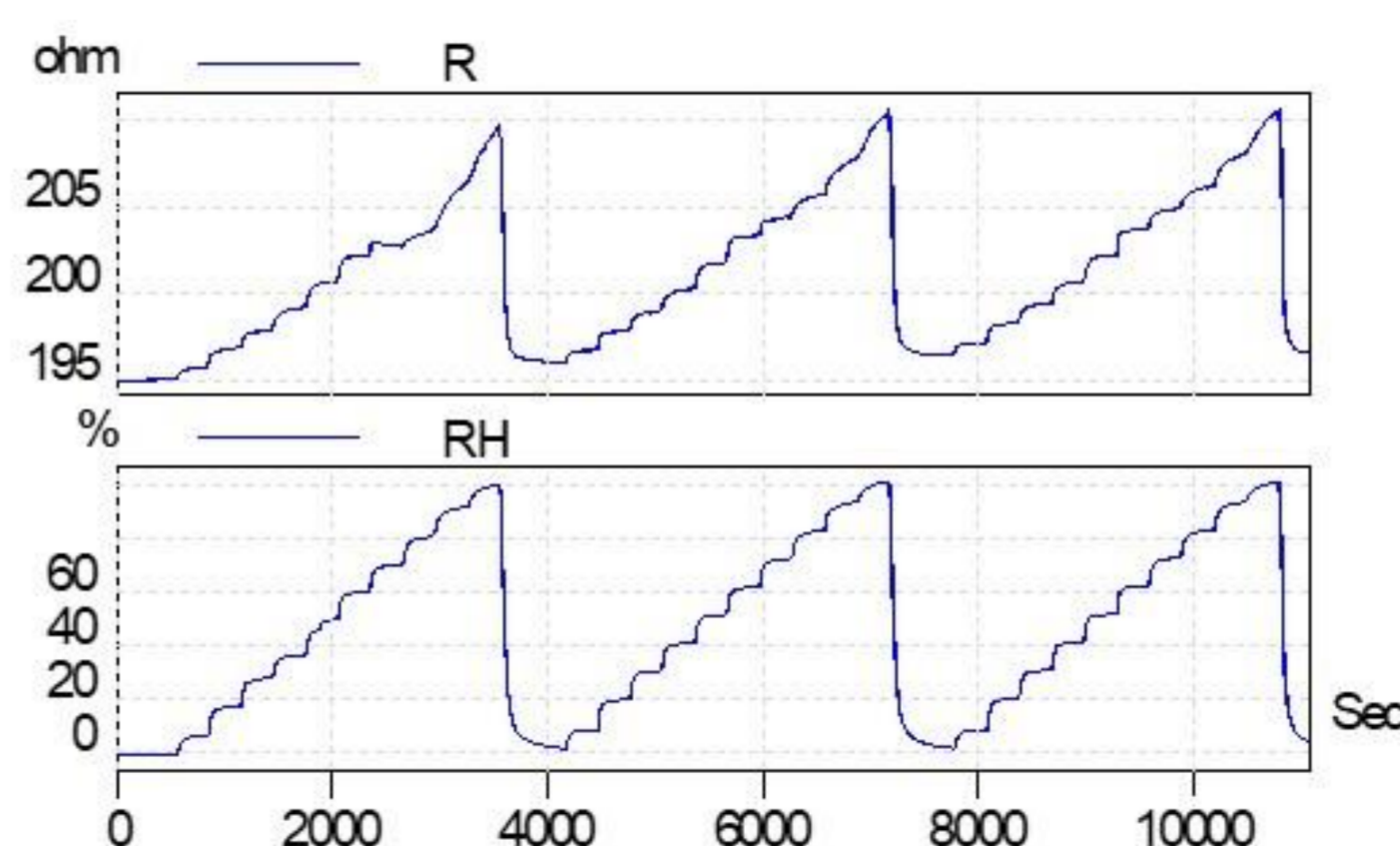


**FIG 3 -** SEM image for  
 $CNH_{OX}/SnO_2/ZnO/PVP$   
at 1.5/1/1/1 nanohybrid  
composition



**FIG 4 –** R Curve: Response of the  
sensor employing  
 $CNH_{OX}/SnO_2/ZnO/PVP$  at 1.5/1/1/1 as  
sensing layer

RH Curve: Response of Sensirion RH  
sensor



**FIG 5 –** R Curve:  
Response of the  
sensor employing  
 $CNH_{OX}/SnO_2/ZnO/PVP$   
at 3/1/1/1 as sensing  
layer  
RH Curve: Response  
of Sensirion RH sensor

## CONCLUSIONS

- The IDT sensing structure presented in this work exhibits a linear response and good RH sensitivity when varying RH from 0% up to 90% in humid  $N_2$  environment. The sensor response time and stability are comparable to that of a commercially available RH sensor.

## ACKNOWLEDGMENT

- This work was funded by the Romanian Ministry for Research and Innovation, through the PN 1916/2019 - MICRO-NANO-SIS PLUS / 08.02.2019 Program