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Nanocasting synthesis of mesoporous SnO_2 for humidity sensor application

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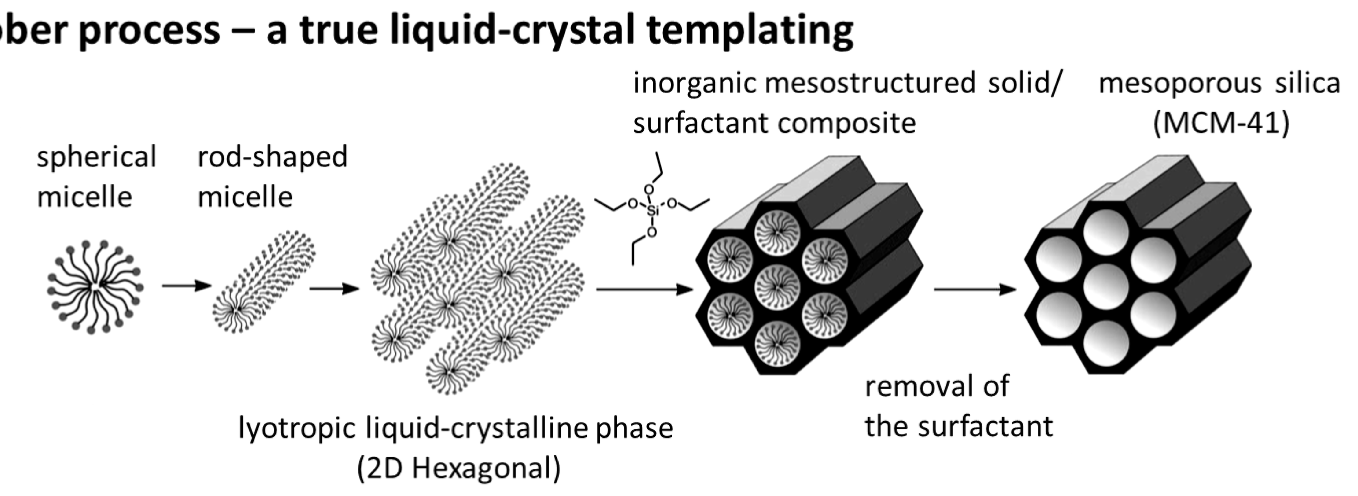
Abstract

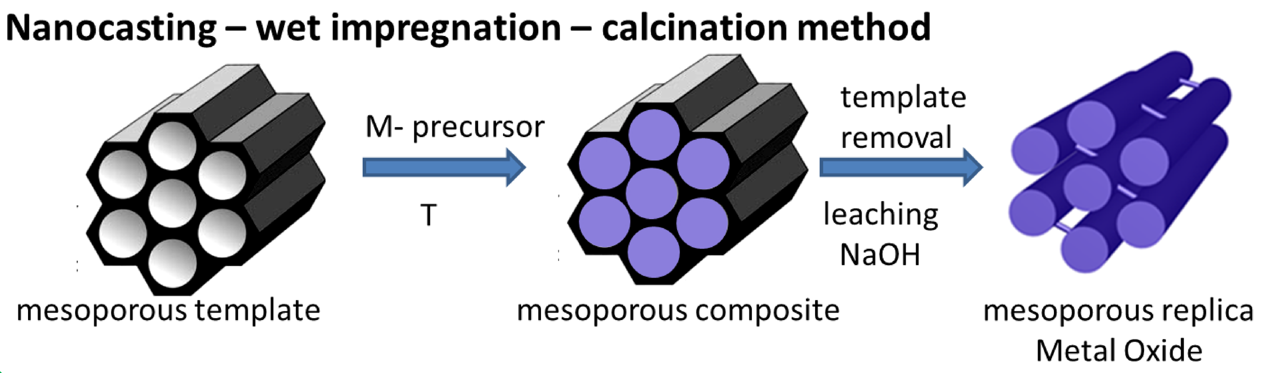
This work presents the fabrication of humidity sensor based on SnO_2 sensing material derived by nanocasting process using hydrothermally obtained KIT-5 as a hard template. In a typical wet impregnation process, the infiltration of Sn precursor into mesoporous silica KIT-5, and later evaporation of the solvent were conducted to fill pores to 15 % of the template pore volume. The calcination and removal of the template were performed to obtain the desired mesoporous SnO_2. The obtained powder (P) was mixed with a 10 % ethyl-cellulose in α- terpineol solution (S) and acetic acid (A) in the weight ratio P:S:A=7:69.7:23.3 to form a homogeneous paste which was further deposited by doctor blade technique onto alumina substrate with screen printed Pt/Ag electrodes. The film was subjected to a specific drying regime and finally thermally treated at 500 °C for 60 minutes. The obtained SnO_2 nanoparticles as well KIT-5 template were characterized using X-ray diffraction (XRD) spectroscopy, Brunauer–Emmett–Teller (BET) analysis and Transmission Electron Microscopy (TEM). The humidity sensing properties of the mesoporous SnO_2 sensor were investigated in a JEIO TECH TH-KE-025 temperature and humidity climatic chamber in the range 30–90 % RH. Complex impedance spectra of the as-fabricated sensor were analyzed at room temperature and 50 °C with a HIOKI 3532-50 LCR HiTESTER in a frequency range 42 Hz - 1 MHz.

Experimental

I Stöber process – a true liquid-crystal templating



II Nanocasting – wet impregnation – calcination method



KIT-5 synthesis with 3-D close-packed cage-type Fm3m mesostructure

synthesis in low acid media

Amphiphilic triblock copolymer, F 127 (a structure directing agent)

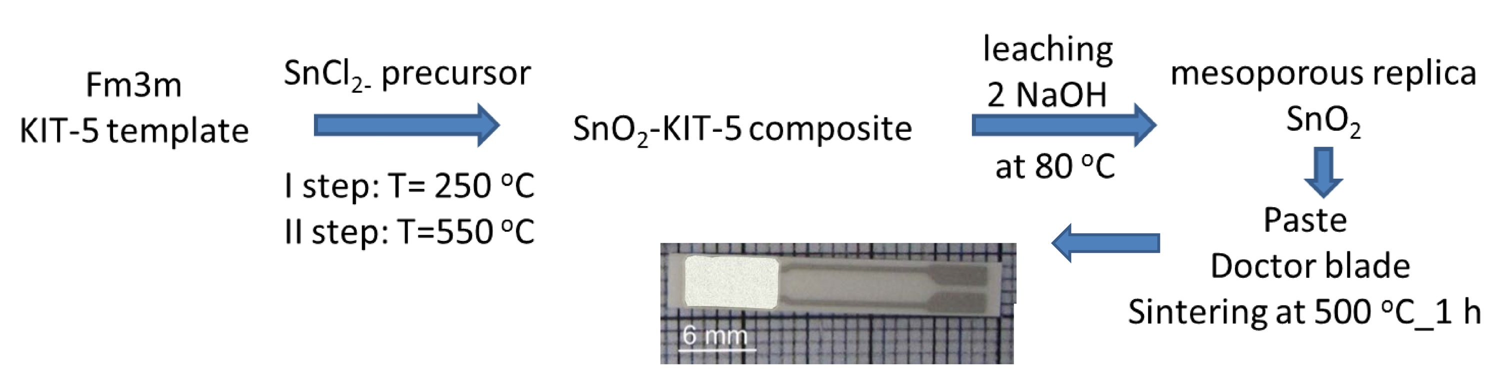
tetraethoxysilane, TEOS, silica source

Reaction mixture molar composition: TEOS:F $_{127}$:HCl:H_2O=1:0.0035:0.88:119

- stirred @ 45 °C (24h) →mesostructured product
- hydrothermally treated @ 130°C (24h)

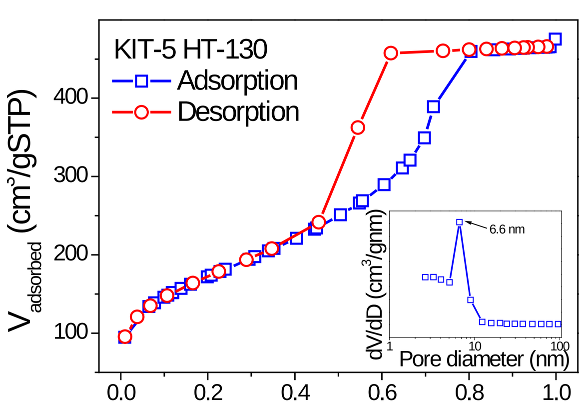
→ the tailoring of SSA and $D_{mesopore}$

II Nanocasting – wet impregnation – calcination method

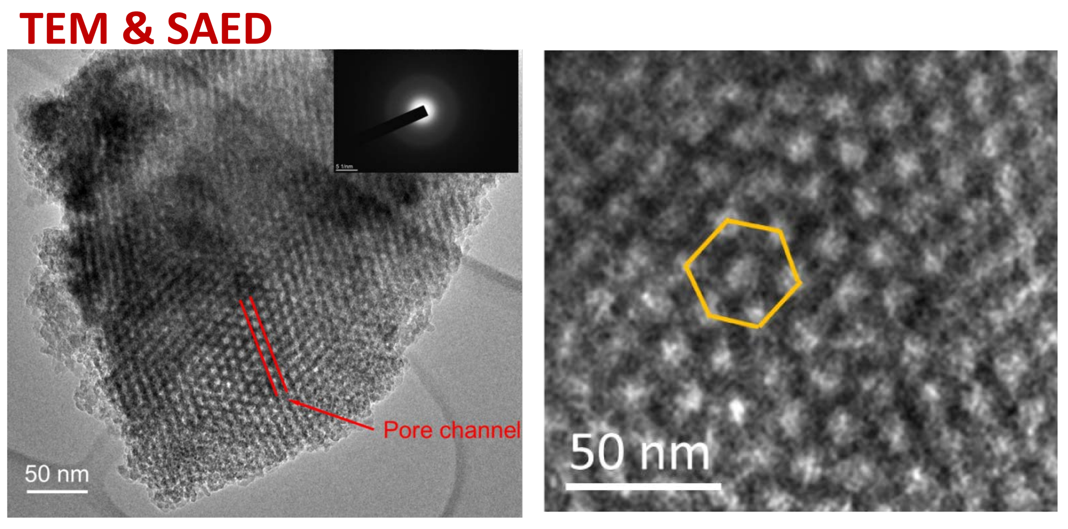


Results

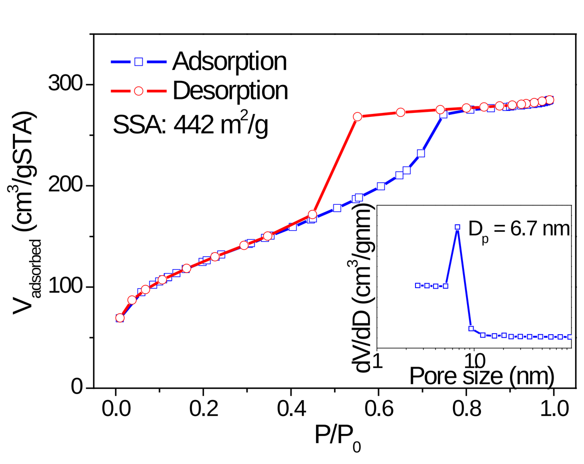
BET & BJH

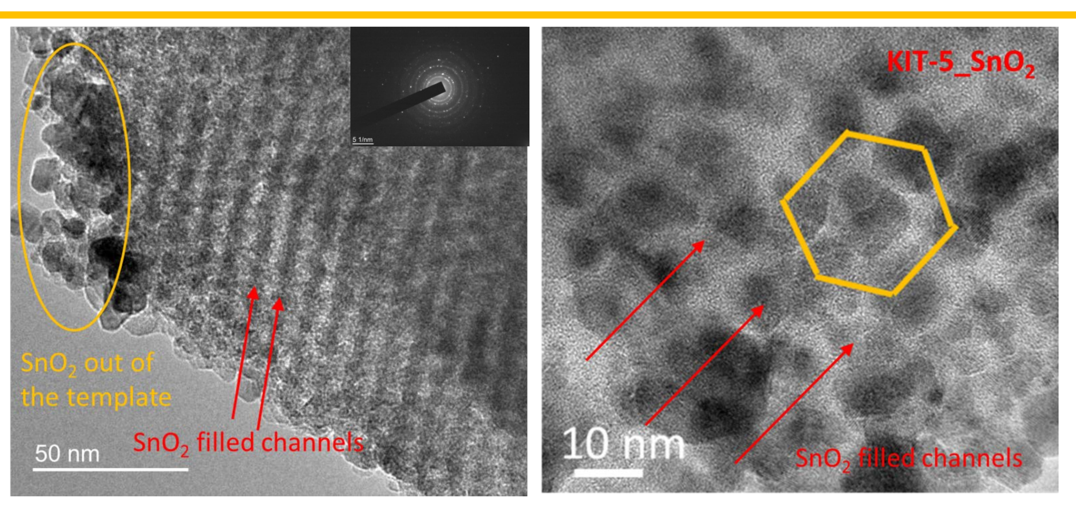


TEM & SAED

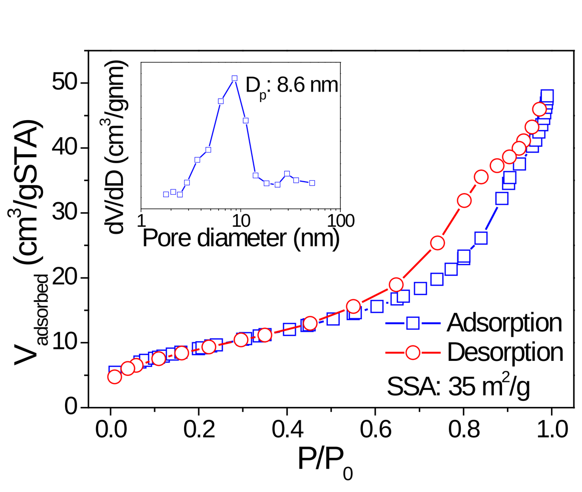


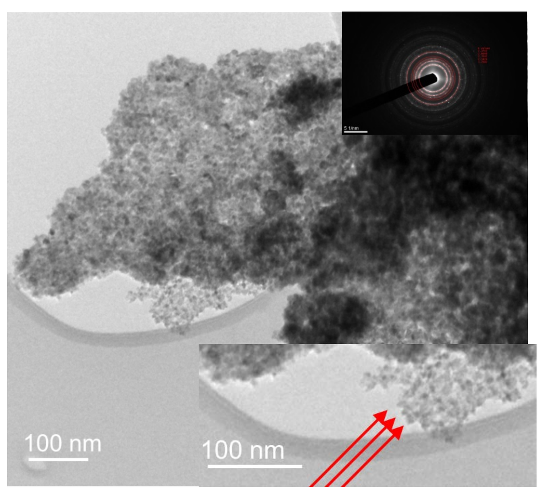
Specific surface area, pore diameter and uniform pore channels with long range order of the **KIT-5** .

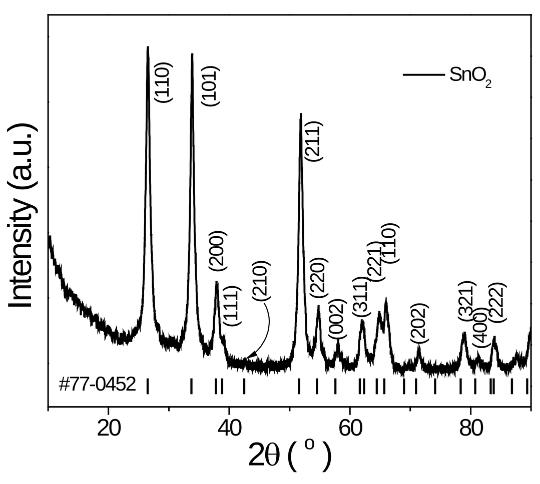




Specific surface area, pore diameter and SnO_2 filled pore channels of the **KIT-5-SnO_2** hybrid.







Template-free SnO_2 sample: Specific surface area, pore diameter, confirmation of crystallinity (XRD, SAED) and mesoporosity (TEM).

Sample	RH (%)	Order of impedance change	Response (s)	Recovery (s)	Hysteresis (%)
[1]ordered-SnO_2	11-96	2	32	42	< 5
[2]SnO_2-$SBA15_{WI}$	11-98	4.5	33	50	2.9
[3]In-SnO_2/mesoCN	11-96	5	3.5	1.5	1
This work	40-90	3	4	6	3.7

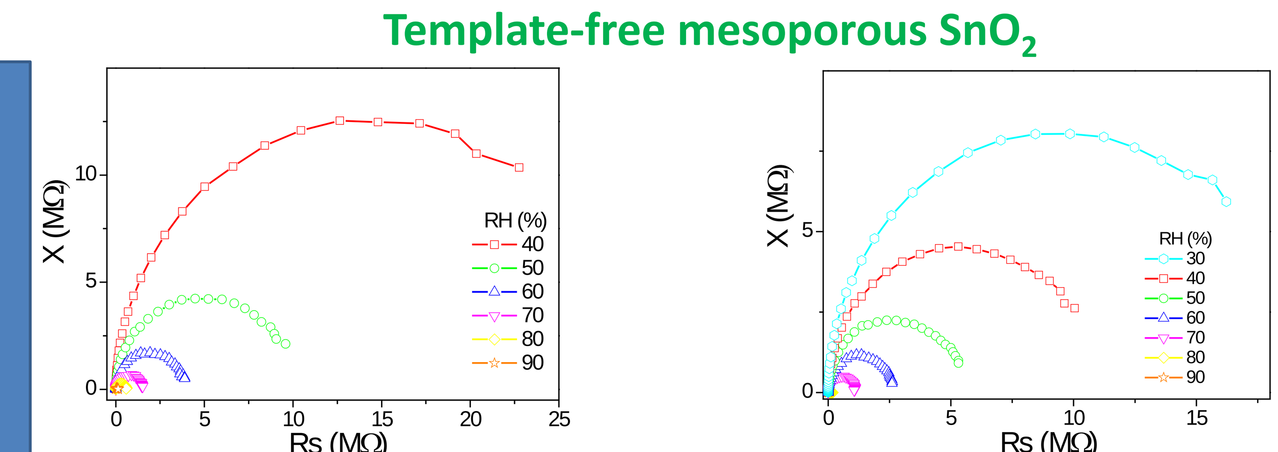
[1]W. Li et al., *Sensors* **17** (2017) 2392.
[2]V. K. Tomer et al., *Sensors and Actuators B* **212** (2015) 517.
[3]R. Malik et al., *J. Mater. Chem. A* **5** (2017) 14134.

Sensor response to humidity

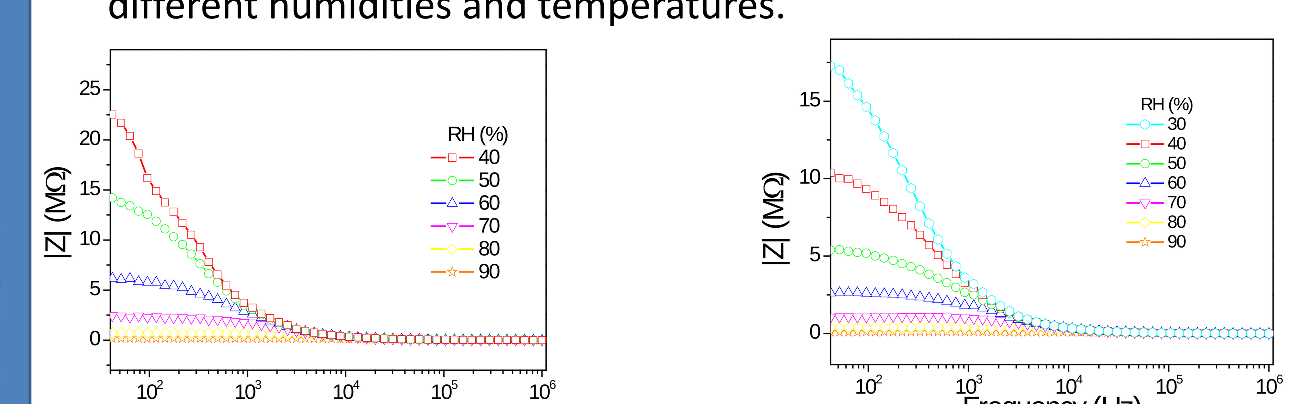
Template-free mesoporous SnO_2

T = 25 °C

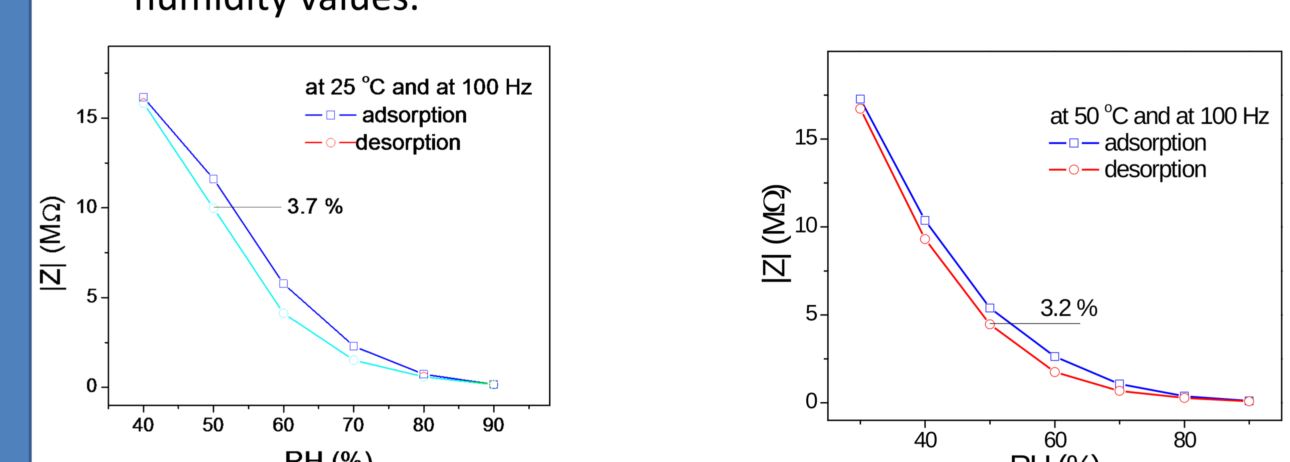
T = 50 °C



Complex impedance spectra of the mesoporous SnO_2 measured at different humidities and temperatures.

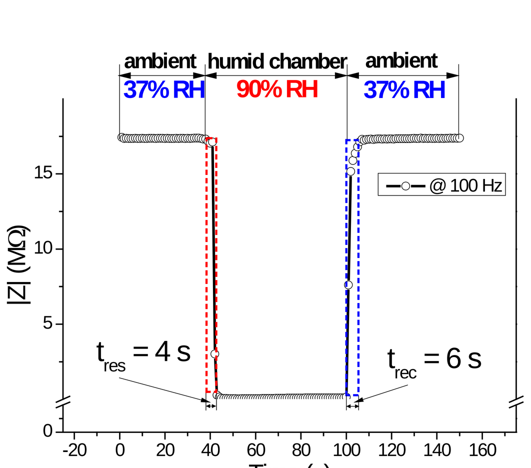


Change of impedance with frequency at 25 and 50 °C for different humidity values.

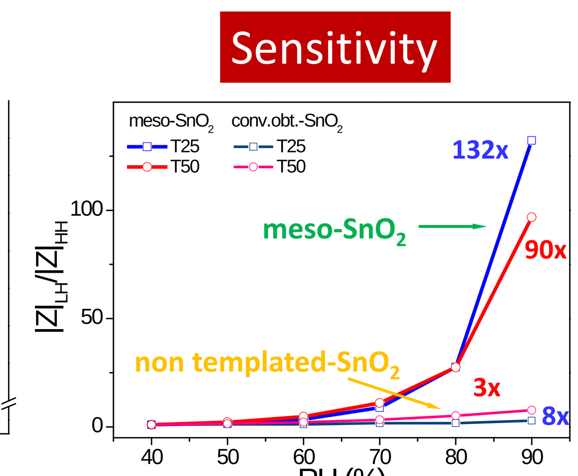


Hysteresis curves showing adsorption-desorption responses measured in the 40-90 RH% at 25 °C and 50 °C.

Response/Recovery



Sensitivity



Conclusion

- Nitrogen adsorption isotherms of KIT-5 showed high specific surface area of 610 m^2g^{-1} and average pore diameter of 6.6 nm while those values for SnO_2 sample were 35 m^2g^{-1} and 6.7 nm respectively.
- Selective area diffraction analysis of template-free sample display well defined rings typical for cassiterite SnO_2.
- The impedance measured at 100 Hz, at room temperature, and in the range 40-90% RH reduced 132 times, while at 50 °C it reduced 90 times.
- The sensor exhibited quick response (4 s) and recovery time (6 s) when it exposed to humidity change from 37% RH to 90% RH, and relatively low hysteresis of 3.7% observed above 50% RH and at room temperature showing its promising capacity as a humidity sensor.