



## Research Paper

Yolk-shelled  $\text{ZnCo}_2\text{O}_4$  microspheres: Surface properties and gas sensing application

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## ABSTRACT

The need to improve the sensitivity, selectivity and stability of ozone gas sensors capable of monitoring the environment to prevent hazard to humans has sparked research on binary metal oxides. Here we report on a novel ozone gas sensor made with ca. 0.5  $\mu\text{m}$  yolk-shelled  $\text{ZnCo}_2\text{O}_4$  microstructures synthesized via an eco-friendly, co-precipitation method and subsequent annealing. With these  $\text{ZnCo}_2\text{O}_4$  microspheres, ozone concentrations down to 80 parts per billion (ppb) could be detected with a.c. and d.c. electrical measurements. The sensor worked within a wide range of ozone concentrations, from 80 to 890 ppb, being also selective to ozone compared to  $\text{CO}$ ,  $\text{NH}_3$  and  $\text{NO}_2$ . The high performance could be attributed to the large surface area to volume ratio inherent in yolk-shell structures. Indeed, ozone molecules adsorbed on the  $\text{ZnCo}_2\text{O}_4$  surface create a layer of holes that affect the conductivity, as in a p-type semiconductor. Since this mechanism of detection is generic,  $\text{ZnCo}_2\text{O}_4$  microspheres can be further used in other environment monitoring devices.

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## 1. Introduction

Monitoring toxic and harmful gases is now considered essential all over the world [1–5], owing to the increasing release of harmful gases, liquids and chemicals from industrial effluents, agricultural chemicals and fertilizers [6]. Toxic air pollutants such as  $\text{CO}$ ,  $\text{NO}_2$  and  $\text{NH}_3$  have been detected with chemiresistor gas sensors based on metal oxides [7,8], which still require improvements to reach the selectivity needed for practical applications [9]. Ozone ( $\text{O}_3$ ) is a potentially harmful gas that has received less attention, in spite of its effects on the human respiratory system that may cause loss of consciousness [6]. Continuous monitoring ozone in the environment is therefore important [10,11], as exposure to ozone levels above 120 ppb should be avoided, according to European Guidelines (2002/3/EG) [12,13]. Sensors made with metal semicon-

ducting oxides are normally incapable to meet the requirement of detecting ozone at the ppb level [14]. There are exceptions though, including some n-type semiconductors, viz.  $\text{ZnO}$  [15],  $\text{SnO}_2$  [16],  $\text{WO}_3$  [17],  $\alpha\text{-AgWO}_4$  [18],  $\text{NiCo}_2\text{O}_4$  [19] and  $\text{In}_2\text{O}_3$  [20], especially the nanocrystalline  $\text{In}_2\text{O}_3$  films able to operate at room temperature and detect ozone levels down to 15 ppb [21]. Despite the high sensitivity of the latter n-type semiconductor sensors, issues have to be addressed to improve stability and decrease response and recovery times [22]. Even more challenging is to achieve such high sensitivity if sensors based on p-type semiconductors are used [22].

Another possible avenue to enhance sensitivity and stability is to prepare gas sensors with binary metal oxides, which can be produced with a variety of methods, including hydrothermal [23–26], co-precipitation/digestion [27,28], microemulsion [29], template-assisted synthesis [30,31], pyrolysis [32,33], solvothermal [34–37] and thermal decomposition [38,39] methods. The resulting binary metal oxides ( $\text{AB}_2\text{O}_4$ ) may adopt shapes such as nano/microflowers, nanowires, nanoarrays, nanorods, and hollow microspheres [40]. Gas sensors with these binary oxides have been used for detection of carbon monoxide, Liquefied Petroleum Gas

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(LPG), chlorine, ethanol, formaldehyde [27,29,30,33,41] in addition to ozone with p-type hexagonal platelets [19].

In this study, we build upon the successful use of binary metal oxides for sensing, now employing binary oxides made of cobalt and zinc. This choice was motivated by the high electronic conductivity and electrochemical activity of zinc cobalt oxide ( $\text{ZnCo}_2\text{O}_4$ ) used in Li-ion batteries [42] and as a hole transport layer in organic photovoltaics (PVs) [43]. Nanostructured  $\text{ZnCo}_2\text{O}_4$  in distinct shapes has been used to detect volatile organic compounds (VOCs) [29,30], such as methanol, formaldehyde, acetone and ethanol [22,34,44]. Here, we report on the use of  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres, synthesized in a cost-effective, eco-friendly co-precipitation method, for detecting ozone with electrical measurements. Significantly, a high sensitivity was reached with the high surface area to volume ratio inherent in yolk-shell structures.

## 2. Experimental section

The chemical reagents zinc (II) acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (99%)), cobalt (II) acetate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (99%)), and ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ , A.R.) were supplied by Sigma-Aldrich Co. LLC. and used without any further purification.

### 2.1. Synthesis of $\text{ZnCo}_2\text{O}_4$ yolk-shell microspheres

The  $\text{ZnCo}_2\text{O}_4$  compound was synthesized using the co-precipitation method [45], in which  $\text{ZnCo}_2\text{O}_4$  microspheres were prepared by dissolving 2 mM of zinc acetate and 4 mM of cobalt acetate in 50 mL ethylene glycol (EG), left under vigorous stirring for 30 min. This homogeneous solution was then transferred to a glass container, which was kept in an oil bath for 2 h at 170 °C, followed by cooling down to room temperature. The precipitate powder was washed several times with deionized water, ethanol and acetone. This powder was then dried in a vacuum oven overnight at 80 °C, after which it was heated in an electric furnace to 350 °C at a heating rate of 1 °C  $\text{min}^{-1}$  during 5 h, leading to crystalline  $\text{ZnCo}_2\text{O}_4$  powder. The synthesis procedure of pristine  $\text{ZnCo}_2\text{O}_4$  is schematically illustrated in Fig. S1 in the electronic Supplementary information.

### 2.2. Material characterization

The crystalline phase of  $\text{ZnCo}_2\text{O}_4$  samples was identified by X-ray diffraction (XRD), using  $\text{CuK}\alpha$  radiation (Rigaku, Rotaflex RU-200B) in the  $2\theta$  range from 10° to 80° with a step of 0.02° and step scanning of 2°  $\text{min}^{-1}$ . The morphological characteristics of  $\text{ZnCo}_2\text{O}_4$  microspheres were analyzed by field emission scanning electron microscopy (FE-SEM, Zeiss Sigma) operating at 5 kV, equipped with X-ray energy dispersive spectroscopy (EDS). Sample cross-sections were obtained in a dual-beam microscope (FEI Helios NanoLab 600i). The phase and crystallinity of  $\text{ZnCo}_2\text{O}_4$  were further investigated using transmission electron microscopy (TEM; Philips, CM200) operated at 200 kV. Thermo-gravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (Perkin Elmer TGA7) at a scan rate of 10 °C  $\text{min}^{-1}$  in air. The specific surface area and pore size distribution of the material were estimated using the Brunauer-Emmett-Teller (BET) method based on the nitrogen adsorption-desorption isotherms (BELSORP-mini II, Japan). The composition and chemical state of the final products were analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCALAB-MKII spectrometer (UK) with Al  $\text{K}\alpha$  radiation (1486.6 eV) as the X-ray source for excitation. The binding energies (BEs) were evaluated using C1s spectrum (BE = 284.6 eV) as the reference with an accuracy of  $\pm 0.1$  eV.

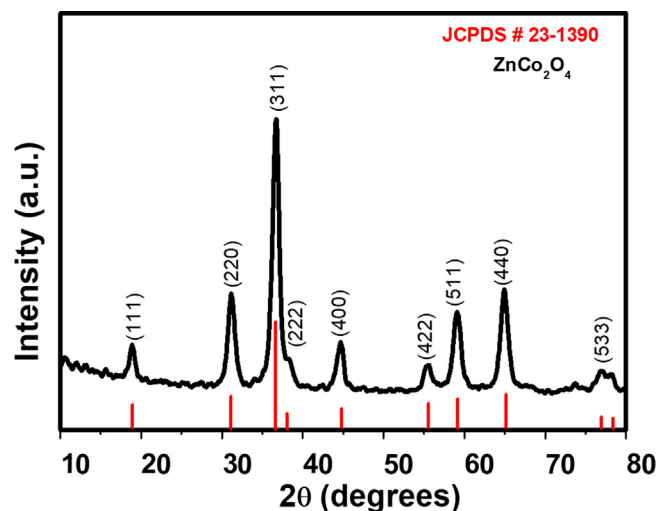


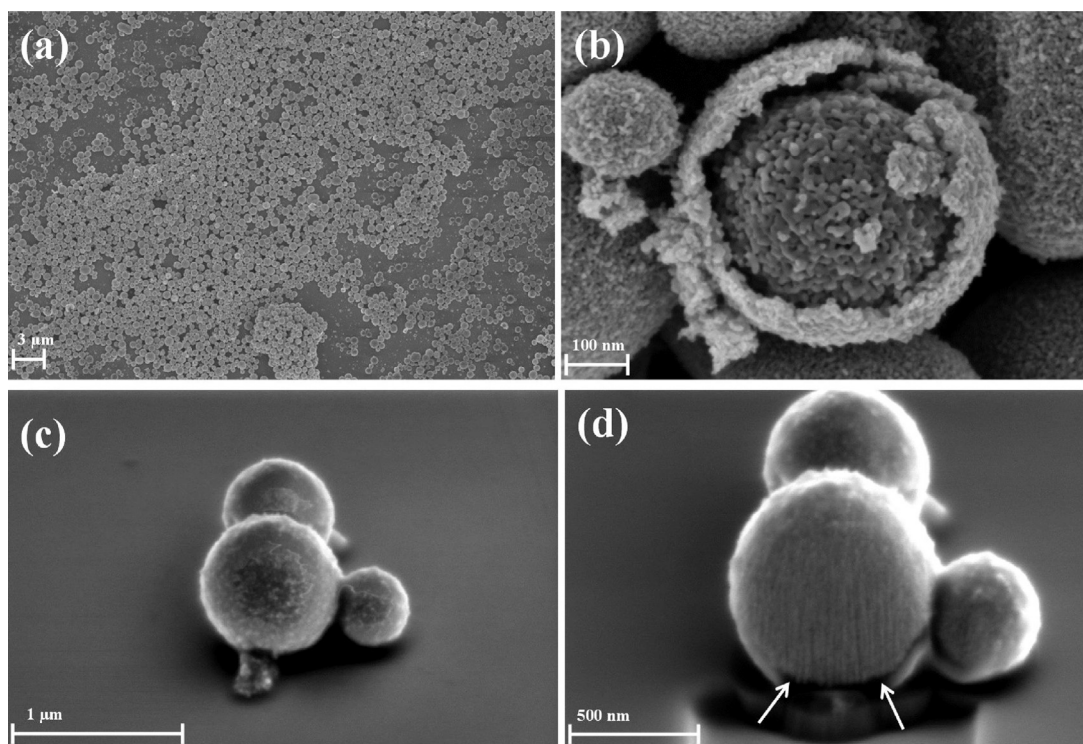
Fig. 1. XRD pattern of  $\text{ZnCo}_2\text{O}_4$  annealed at 350 °C for 5 h in ambient atmosphere.

### 2.3. Fabrication of $\text{ZnCo}_2\text{O}_4$ sensing film and gas-sensing measurements

Gas sensing devices were fabricated by ultrasonically dispersing the as-prepared  $\text{ZnCo}_2\text{O}_4$  powders (10 mg) in 1 mL isopropyl alcohol and the suspension was then drop-cast onto a  $\text{SiO}_2/\text{Si}$  substrate containing 100 nm thick Pt electrodes separated by a distance of 50  $\mu\text{m}$ . Details of preparation of the interdigitated electrodes (IDEs) are given in [19]. After dropping the  $\text{ZnCo}_2\text{O}_4$  solution, the substrates were heated to 100 °C for 10 min to evaporate the solvent, followed by calcination at 350 °C for 2 h in an electric furnace in air to stabilize the sample before the gas sensing measurements. Pictures of the system to measure the chemiresistive gas sensing performance are shown in Fig. S2. The sensor was inserted into a chamber with temperature control from 100 to 300 °C under different ozone concentrations. Dry air was used as both the reference and the carrier gas for all measurements, with a constant total flow of 500 SCCM kept via mass flow controllers. Ozone gas was formed by oxidation of oxygen molecules of dry air with a pen-ray UV lamp (UVP, model P/N 90-0004-01), which was calibrated using a toxic gas detector (ATI, model F12) that provided ozone level concentration in the range of 80–890 ppb. The applied DC voltage was 1 V and the electrical resistance was measured using an electrometer Keithley (model 6514). The ozone-containing dry air was blown directly onto the sample, which was placed in a heated holder system. For gas sensing characterization, the sensors were exposed to 1 ppm (parts-per-million) of various gases, namely nitrogen dioxide ( $\text{NO}_2$ ), carbon monoxide (CO) and ammonia ( $\text{NH}_3$ ) controlled by mass flowmeters. Details of the gas-sensing experiments are available in [46]. The sensor response was calculated from the response curves using Eq. (1):

$$\text{Sensor Response (\%)} = \left| \frac{\Delta R}{R_a} \right| \times 100 \quad (1)$$

where  $\Delta R = R_a - R_g$  for oxidizing gases like ozone, and  $R_g$  and  $R_a$  are the electrical resistances of the sensor film with target gases and dry air, respectively. The response and recovery times were defined as the time needed for reaching 90% of total change in resistance upon exposure to the target gas and fresh air, respectively. During the measurements, the relative humidity was kept within the range 30–50% RH (Termo-Higrometro model HT-700). The AC Impedance spectroscopy data were obtained with the  $\text{ZnCo}_2\text{O}_4$  film using an impedance/gain-phase analyzer (Solartron SI 1260) in the frequency range from 1 Hz to 1 MHz at an operating temperature of 200 °C.



**Fig. 2.** (a and b) FE-SEM images with different magnifications of  $\text{ZnCo}_2\text{O}_4$  annealed at  $350^\circ\text{C}$  for 5 h. (c) As deposited and (d) FIB-sectioned  $\text{ZnCo}_2\text{O}_4$  sample displaying the yolk and the shell parts.

### 3. Results and discussion

#### 3.1. Structural and microstructural characterizations

$\text{ZnCo}_2\text{O}_4$  yolk-shelled microspheres were synthesized via an eco-friendly precipitation route without any surfactant. Fig. S3 shows the thermogravimetric analysis (TGA) curve of  $\text{ZnCo-glycolate}$  precursor which indicates a total weight loss of 45.5% above  $300^\circ\text{C}$ . Two major weight loss steps were identified: the first loss of  $\sim 12\%$  up to  $210^\circ\text{C}$  is attributed to the release of chemically and physically adsorbed ethylene glycol and other organic molecules, while the other major weight loss of 33.5% is attributed to thermal decomposition of  $\text{ZnCo-glycolate}$  into  $\text{ZnCo}_2\text{O}_4$ . Above  $300^\circ\text{C}$  no weight loss was observed, which confirms the formation of pure  $\text{ZnCo}_2\text{O}_4$  phase. To ensure complete decomposition of the precursor, we chose  $350^\circ\text{C}$  as the calcination temperature for the synthesis of  $\text{ZnCo}_2\text{O}_4$ .

Fig. 1 displays the XRD pattern of  $\text{ZnCo}_2\text{O}_4$  powder annealed for 5 h at  $350^\circ\text{C}$ , where all reflections were indexed to a face-centered-cubic (fcc) arrangement with Fd3m (227) space group (JCPDS file No. 23-1390) and spinel structure, by comparing with the standard pattern illustrated by the vertical red lines.

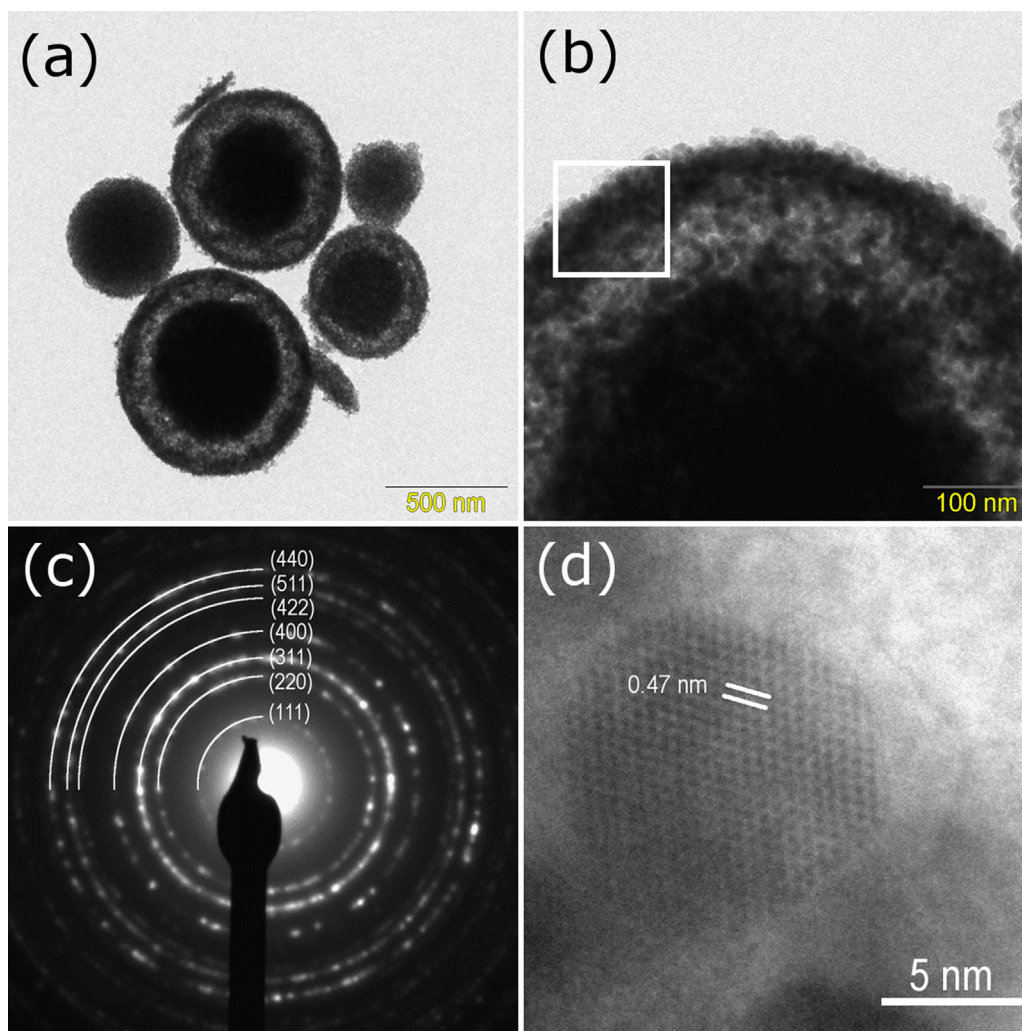
The hysteresis on the  $\text{N}_2$  adsorption–desorption isotherms for the yolk-shelled  $\text{ZnCo}_2\text{O}_4$  in Fig. S4 is classified as type III, with a type  $\text{H}_4$  hysteresis loop, according to IUPAC (International Union of Pure and Applied Chemistry). These are typical of mesoporous materials formed by agglomerated particles [47]. The BET specific surface area was  $52.73\text{ m}^2\text{ g}^{-1}$ , with a pore volume of  $0.10\text{ m}^3\text{ g}^{-1}$ . The pore size distribution, derived from desorption data and estimated from the isotherm using the Barrett–Joyner–Halenda (BJH) model (inset in Fig. S4), indicates a pore diameter ranging from 5 to 91 nm, with an average of 10 nm. This mesoporous structure is beneficial to sensing because the target gas molecule easily penetrates into the pores, thus leading to a larger analyte/sample contact area

and providing interconnected paths that facilitate electron transport and accelerate species diffusion [48,49].

Fig. 2(a) shows the spherical-like morphological features of  $\text{ZnCo}_2\text{O}_4$  in the FE-SEM images, which are preserved upon calcination. A typical broken yolk-shelled microsphere is shown in Fig. 2(b). The core of the material is highly porous and composed of polycrystalline nanosized particles, in good agreement with BET results. The formation process of yolk-shelled microspheres is due to Ostwald ripening by minimization of surface energy [45]. In the synthesis,  $\text{ZnCo-glycolate}$  is formed due to interlinking of ethylene glycol at  $170^\circ\text{C}$ ; owing to a high surface energy and aggregation it turns into spheres with reduced free energy [45,50]. The yolk-shelled structure arises from the heat treatment during thermal decomposition of  $\text{ZnCo-glycolate}$  under non-equilibrium conditions. As the temperature reaches  $350^\circ\text{C}$  during calcination, the  $\text{ZnCo-glycolate}$  core starts to decompose into  $\text{ZnCo}_2\text{O}_4$ , thus eventually leading to a  $\text{ZnCo}_2\text{O}_4$  yolk-shelled microsphere [45]. Fig. 2(c) illustrates the typical yolk-shell spheres while Fig. 2(d) shows the cross-section of the larger sphere made by FIB (Focused Ion Beam), confirming the small yolk surrounded by a thin shell (white arrows in Fig. 2(d)). The purity of the as-obtained  $\text{ZnCo}_2\text{O}_4$  particles is ensured by the EDS mapping images in Fig. S5, where there are only Zn, Co and O elements uniformly distributed throughout the structure, in addition to Si from the substrate.

The gap between the outer shell and the inner yolk in the microspheres is illustrated in the low and high magnification TEM images in Fig. 3(a) and (b). Some broken spheres do not possess a shell due to the ultrasound bath used for TEM sample preparation, as observed in Fig. 3(a). Details of a yolk-shell sphere are marked with a white box in Fig. 3(b), featuring a yolk diameter of  $0.5\ \mu\text{m}$  and wall thickness of ca. 50 nm. The selected area electron diffraction (SAED) pattern for spheres annealed at  $350^\circ\text{C}$  in Fig. 3(c) displays concentric rings, characteristic of polycrystalline materials. The diffraction rings are assigned as (111), (220), (311), (400), (422), (511) and (440) planes of the cubic structure of the  $\text{ZnCo}_2\text{O}_4$  phase, consis-





**Fig. 3.** (a and b) Low and high magnification TEM images of the yolk-shell  $\text{ZnCo}_2\text{O}_4$  microspheres. (c) SAED pattern (d) HRTEM image at the edge of a microsphere.

tent with the XRD analysis. Fig. 3(d) shows the high resolution TEM image of a particle at the shell edge (white square region), where the interplanar distance is 0.47 nm, corresponding to the (111) Miller indices of spinel-type  $\text{ZnCo}_2\text{O}_4$  phase.

The chemical elements comprising the  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres are inferred from the XPS spectra in Fig. 4. The survey XPS spectrum in Fig. 4(a) reveals the presence of C, Zn, Co, and O elements, with the absence of impurities. The appearance of the C peak is derived from adventitious carbon species. The high resolution XPS spectra of Zn 2p, Co 2p, and O 1s after Gaussian fitting are shown in Fig. 4(b–d). Two main peaks appear at 1020.8 and 1043.9 eV for Zn 2p in Fig. 4(b), typical of  $\text{Zn}^{2+}$  with the orbits of Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub>, respectively [51]. The well resolved Co 2p spectrum in Fig. 4(c) shows peaks at 779.4 and 794.2 eV assigned to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>, respectively, with spin-orbit splitting of around 15 eV owing to mixed  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions [52–54]. The O 1s XPS spectrum in Fig. 4(d) can be deconvoluted into three peaks. The lower energy peak at 529.2 eV can be attributed to metal-oxygen bonding (oxygen bonding with Zn and Co) in  $\text{ZnCo}_2\text{O}_4$  [54,55]. The second peak at 530.9 eV is assigned to oxygen of surface hydroxyl groups [56–58], while the third peak at 532.3 eV is due to oxygen molecules chemisorbed onto the semiconductor surface [59].

### 3.2. Gas sensing properties

The gas sensing properties of  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres were investigated by measuring the response of a sensor exposed to 560 ppb of ozone at an operating temperature of 200 °C, with different exposure times (15, 30, and 60 s). Fig. 5(a) reveals that  $\text{ZnCo}_2\text{O}_4$  microspheres were sensitive to ozone even for the shortest exposure time (15 s), with no evidence of saturation upon increasing the time. Fig. S6 in the Supplementary material indicates that even after 3 min of exposure to ozone gas, the sample response was not fully saturated and the recovery time became longer than 30 min. The lack of saturation is probably due to the high surface area to volume ratio of the microspheres [60–62] in addition to the insufficient time for the adsorption process to reach equilibrium. The optimum operating temperature was 200 °C, according to Fig. 5(b), similarly to traditional oxide gas sensors [15,63–65]. The reason why a peak in performance appears is as follows: the reaction kinetics of gases with oxygen species chemisorbed on an oxide surface becomes faster with increasing temperatures, but above 200 °C the rate of desorption is higher than for adsorption, thus decreasing the response. Therefore, there is an optimum operating temperature, where adsorption and desorption processes reach equilibrium. We do not expect any structural change during the sensing measurements because the material had been annealed at a higher temperature than the sensing operating temperature

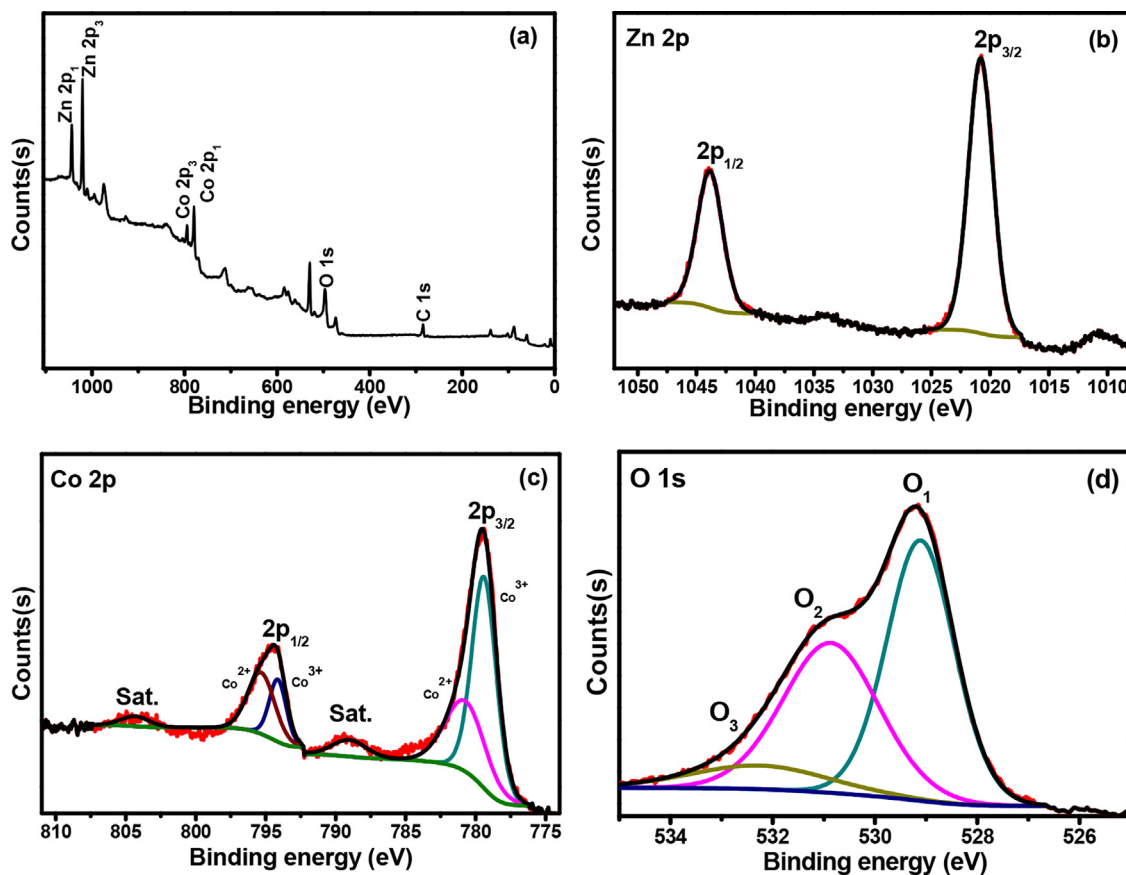


Fig. 4. XPS spectra of the  $\text{ZnCo}_2\text{O}_4$  structure. (a) Survey scan and high resolution scan of (b) Zn 2p, (c) Co 2p, and (d) O 1s regions.

**Table 1**  
Ozone gas sensing parameters for  $\text{ZnCo}_2\text{O}_4$  microspheres at 200 °C.

O <sub>3</sub> level (ppb)	Sensor response (%)	Response time (s)	Recovery time (min)
80	23.3	8.4	9.7
290	35.5	12	17
560	55	21	18
890	71	37.4	21

[55,66]. In subsidiary experiments we found that  $\text{ZnCo}_2\text{O}_4$  yolk-shelled microspheres could detect ozone even at lower operating temperatures, but the recovery time was too long or the original resistance could not be reached back. With regard to the concentration dependence, the response time varied from 8.4 s (80 ppb) to 37 s (890 ppb), while the recovery time varied from 9.7 min (80 ppb) to 21 min (890 ppb) as shown in Fig. 5(c).

It is worth noting that an ozone level above 120 ppb is dangerous to human health, possibly causing problems such as lung damage. The  $\text{ZnCo}_2\text{O}_4$  sensor displays total reversibility and good reproducibility in Fig. 6(a) when exposed to various ozone levels in three measurement cycles. The sample resistance decreased upon exposure to the oxidizing gas, which is indicative of p-type semiconductor behavior. The sensor response increases with ozone concentration and may even not reach saturation for 890 ppb, as indicated in Fig. 6(b). Due to the limitations of our gas sensing system, 80 ppb is the lowest concentration that can be reliably delivered to the sensor device. Table 1 shows the sensing parameters with respect to different ozone levels.

Fig. 7 shows the sensor response of  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres exposed to 1 ppm of reducing (CO and  $\text{NH}_3$ ) and oxidizing ( $\text{O}_3$  and  $\text{NO}_2$ ) gases at an operating temperature of 200 °C. One should note that for reducing gases the change in electrical resis-

tance in Eq. (1) is given as  $\Delta R = R_g - R_a$ . The magnitude of the electrical resistance change was considerably higher for  $\text{O}_3$  (~71%) than for  $\text{NO}_2$  (6.5%),  $\text{NH}_3$  (3.8%) and CO (4.8%). Therefore, the  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres are very selective for ozone, which is promising for sensor devices. The response of this sensor film is also very stable, as indicated by the long-term stability measurements for over 30 days in Fig. S7 (a) and (b) in the electronic Supplementary information.

### 3.3. Impedance spectroscopy measurements of $\text{ZnCo}_2\text{O}_4$ yolk-shell microspheres

The  $\text{ZnCo}_2\text{O}_4$  sensors were also tested for ozone detection through electrical impedance experiments, in concentrations ranging from 80 ppb to 890 ppb at a fixed operating temperature of 200 °C. Fig. 8(a) shows that the impedance data consists of a single semicircle in the Nyquist plot, whose diameter decreases with ozone concentration, consistent with the decreasing resistance upon ozone exposure discussed in the last subsection. In order to obtain further information about the contribution from each region of the sensor, the impedance data were successfully fitted with the equivalent electrical circuit shown in Fig. 9, which also depicts a schematic representation of the sensing sample under ozone flow. Table 2 brings the parameters extracted from data fitting.  $R_b$  refers to the bulk contribution, which manifested here as a non-zero intercept of the impedance data with the real axis towards the highest frequencies; in passing, this parameter did not change under ozone flow. A similar behavior was found for the capacitance  $C_s$ , whose average value was  $0.912 \times 10^{-10}$  F, close to the nF order often observed for surface effects [67,68]. We recall that the system under study contains a yolk-shell-modified particle-to-particle contact surface, the consequence of which is the observation of a

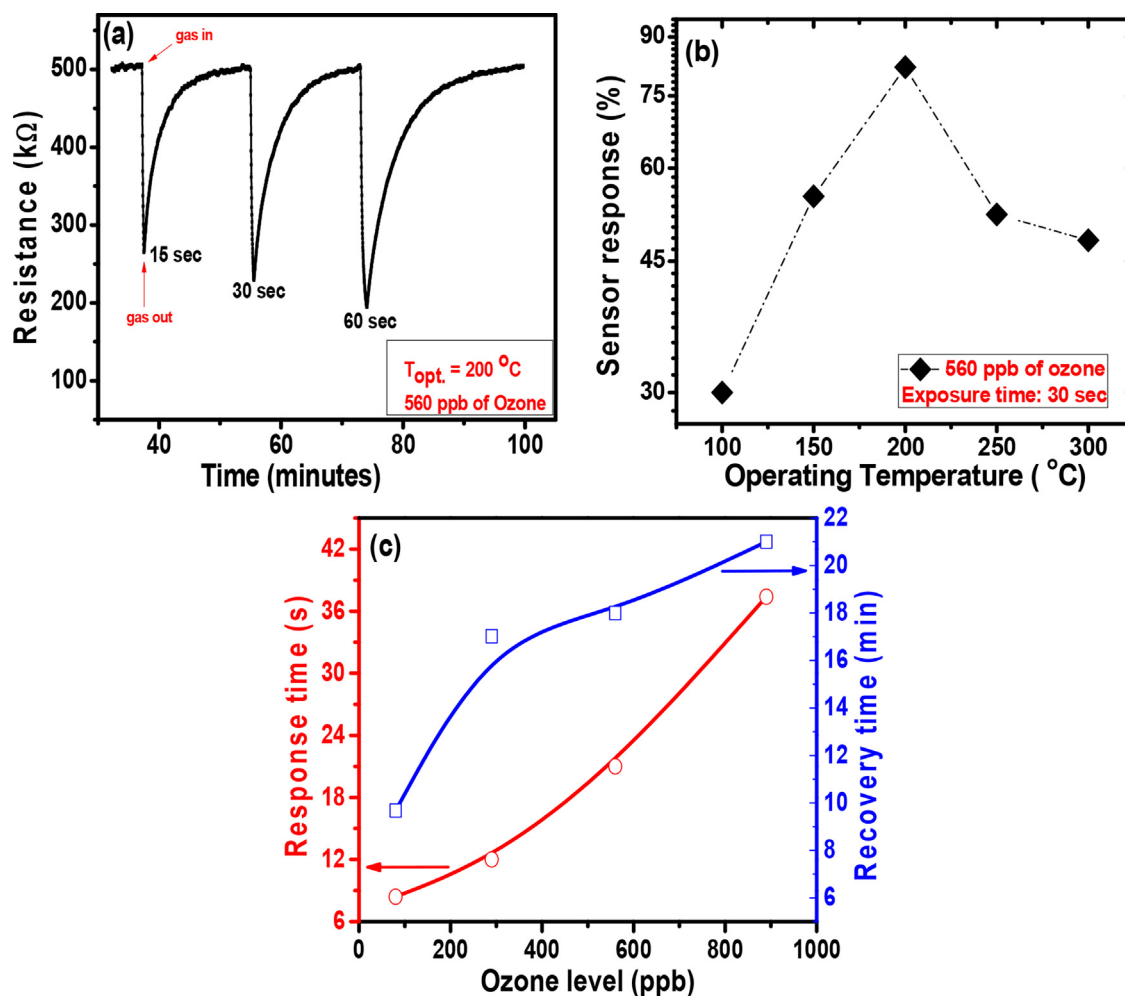


Fig. 5. (a) Dynamic electrical resistance of ZnCo<sub>2</sub>O<sub>4</sub> sample exposed for different periods of time to 560 ppb of O<sub>3</sub> at 200 °C. (b) Sensor response of the ZnCo<sub>2</sub>O<sub>4</sub> sample exposed to 560 ppb O<sub>3</sub> at different operating temperatures. (c) Response and recovery time as a function of ozone concentration from 80 to 890 ppb at 200 °C.

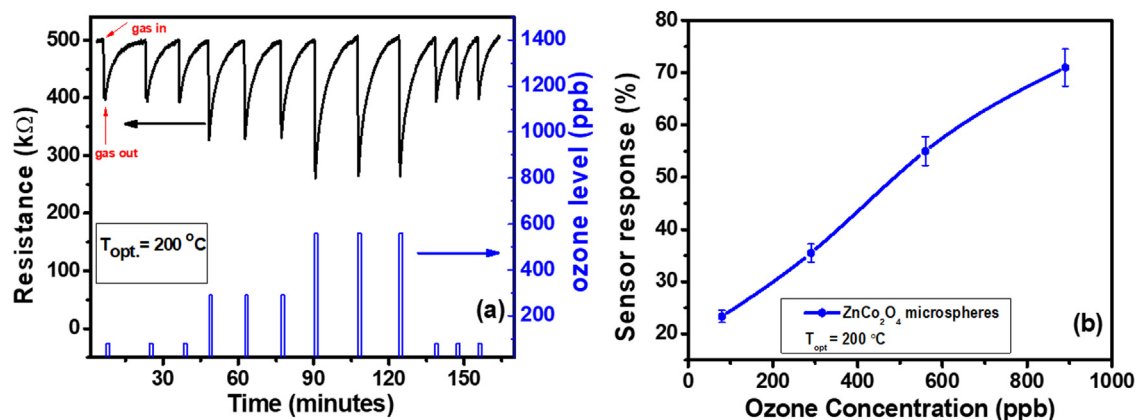


Fig. 6. (a) Dynamic electrical response of ZnCo<sub>2</sub>O<sub>4</sub> sample of three cycles for each ozone concentration (b) Sensor response vs ozone concentration in the range of 80–890 ppb for ZnCo<sub>2</sub>O<sub>4</sub> microspheres at 200 °C.

capacitance value somewhat lower than expected in typical surface effects. The resistance attributed to this surface-like contribution ( $R_s$ ), whose values are shown in Fig. 8(b), decreased with ozone concentration according to an exponential behavior. Note from Table 2 that  $R_s \gg R_b$ , meaning that these contact surfaces act as semi-blocking resistive regions. This is a charge storage effect (i.e., interface polarization of Maxwell-Wagner type [67]), giving rise to the capacitance component observed (impedance semicircle inci-

dence) in Fig. 8(a). The change in impedance calculated from the Nyquist plot by subtracting the spectra before and after ozone exposure is depicted in Fig. 8(c). At high frequencies, the impedance did not vary with ozone concentration, but it did so between 1 Hz and 10 kHz as the electrical response was dominated by surface contributions [69]. It is clear that ozone concentrations well below 80 ppb could be detected, but this was not pursued owing to limitations of the sensor setup. The ozone sensing activity in this material, just

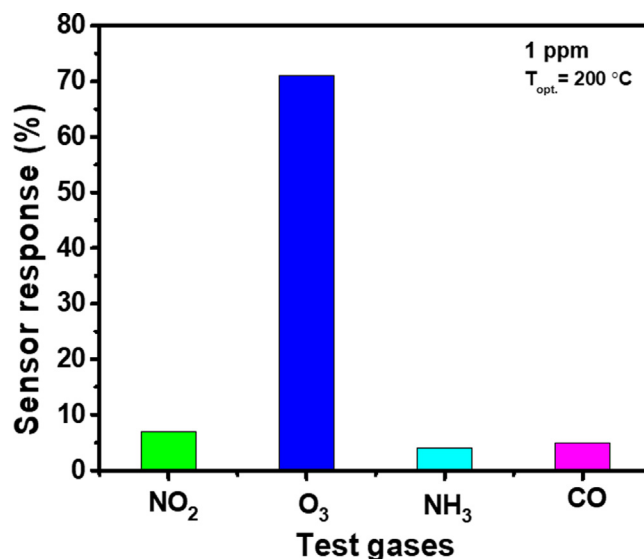


Fig. 7. Selectivity histogram of the  $\text{ZnCo}_2\text{O}_4$  yolk-shell microspheres exposed to common gases present in the atmosphere.

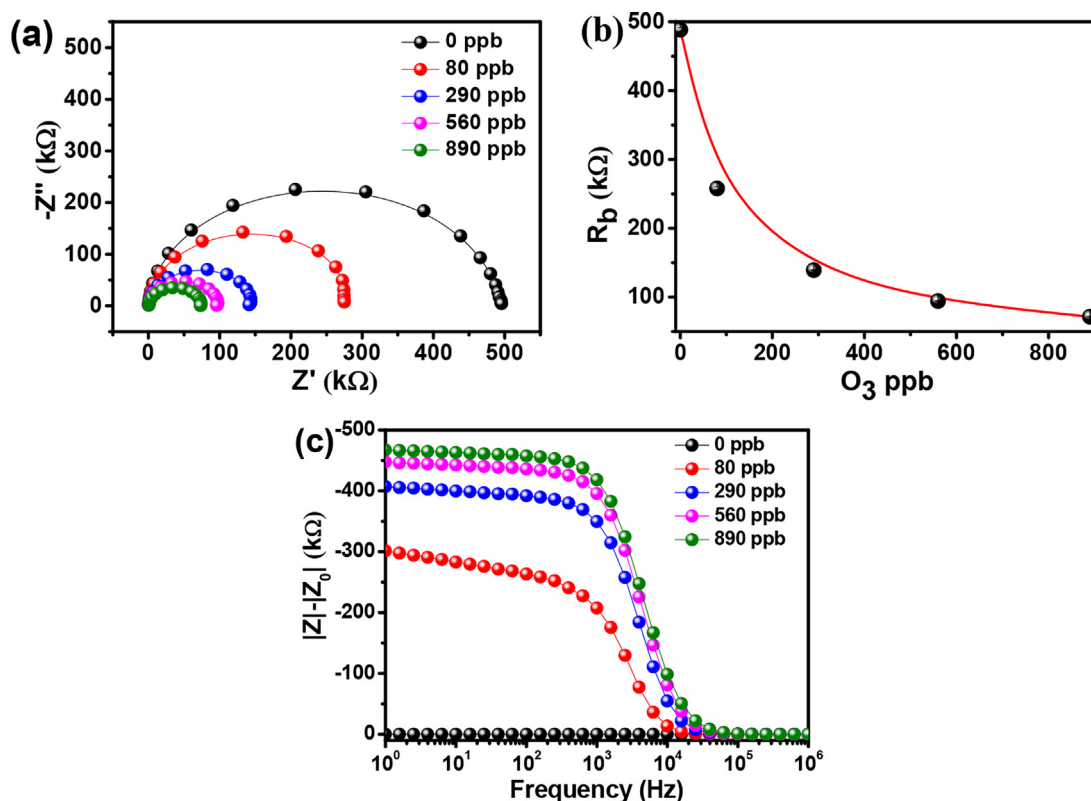


Fig. 8. (a) Nyquist plot of  $\text{ZnCo}_2\text{O}_4$  film in air and after ozone exposure at  $200\text{ }^\circ\text{C}$ . (b)  $R_b$  values from fitting with an equivalent circuit as a function of ozone concentration. (c) Relative magnitude impedance spectra of  $\text{ZnCo}_2\text{O}_4$  sample at  $200\text{ }^\circ\text{C}$  from 1 Hz to 1 MHz for different ozone concentrations.

as found in parent compounds, is shown to be a surface dependent effect, with resistance being the appropriate parameter to monitor. Back to the impedance data in Fig. 8(a) and (c), we found no evidence of contribution from the material-electrode interface to the total impedance at the lowest frequencies. In fact, such a contribution would have involved higher capacitance values, normally approaching  $\mu\text{F}$  order of magnitude, instead of nF [67,68].

The finding above is consistent with an electronic transport mechanism with a non-blocking electrode effect. The adsorbed ozone molecules are expected to act as acceptors while electron trapping on the surface causes band bending, leading to an increase

in free holes near the interface and therefore a decrease in the resistance. The yolk-shell microstructure could be thought of as a filter, where a molecule penetrates the shell and is “trapped” to interact with the inner surface of the shell and the outer surface of the core. Significantly, these yolk-shell microspheres possess high surface area to promote gas adsorption-desorption processes that enhance gas sensing performance.

The whole spectra of normalized magnitude impedance data for all the samples were analyzed with the multidimensional projection technique Interactive Document Map (IDMAP) using the PEx-Sensors software [70–72]. In IDMAP data dimensions are



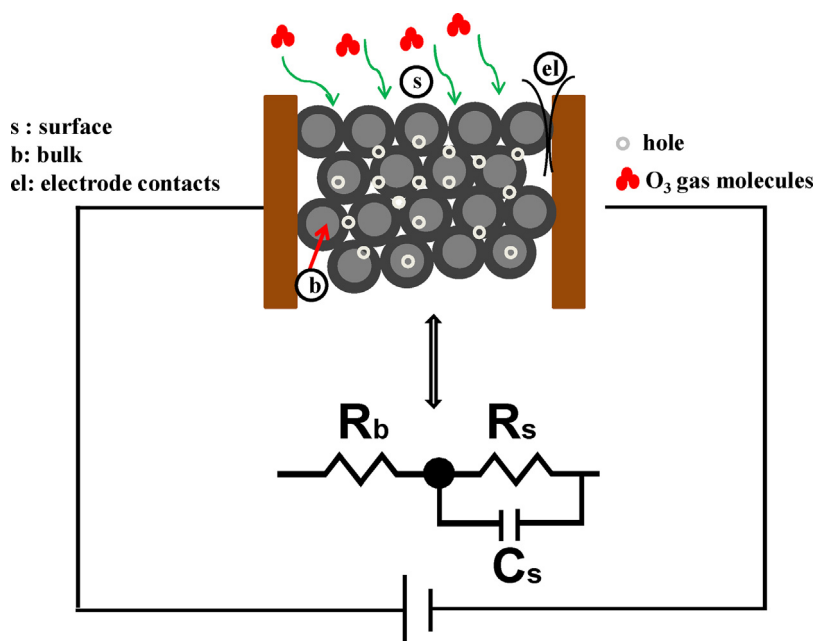


Fig. 9. Schematic representation of the gas sensing material and electrical equivalent circuit to fit the impedance data.

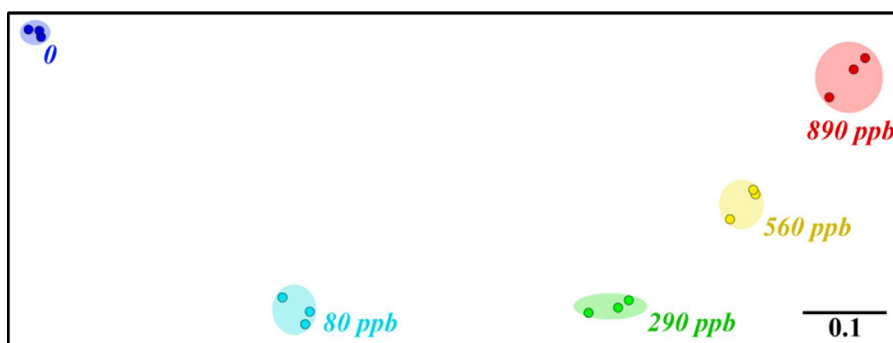


Fig. 10. IDMAP plot of normalized magnitude impedance spectra for different ozone gas concentrations. The scale bar represents the Euclidean distance of 0.1.

Table 2

Parameters from fitting the impedance spectra using an RC equivalent circuit.  $R_b$  is the bulk resistance (volume effect), while  $R_s$  and  $C_s$  are the yolk-shell-modified surface resistance and capacitance contributions to the total impedance.

O <sub>3</sub> (ppb)	$R_b$ ( $\Omega$ )	$R_s$ (k $\Omega$ )	$C_s$ (pF)
0	458.4 ± 37.1	488.7 ± 3.0	90.7 ± 0.7
80	427.5 ± 62.2	258.4 ± 2.6	90.7 ± 1.2
290	442.9 ± 30.2	139.6 ± 0.6	91.0 ± 0.6
560	447.2 ± 26.5	94.7 ± 0.4	91.5 ± 0.6
890	455.7 ± 24.6	71.9 ± 0.3	92.0 ± 0.6

reduced with the Fastmap technique, and then each spectrum was projected as a data point on the projected space. Dissimilarity was defined in terms of Euclidian distances between the spectra. The IDMAP plot in Fig. 10 confirms the efficiency of ZnCo<sub>2</sub>O<sub>4</sub> for ozone sensing, since the distance between the points with no gas to the concentration 80 ppb is large. Quantitatively, this distinguishing ability was represented by a silhouette coefficient of 0.91 [70], to be compared with the maximum value of 1.0.

#### 4. Conclusion

We have shown that ZnCo<sub>2</sub>O<sub>4</sub> microspheres can be synthesized by co-precipitation and subsequent annealing. The structure, morphology and composition of the ZnCo<sub>2</sub>O<sub>4</sub> were confirmed with

several methods, namely XRD, FE-SEM, TEM and XPS. The yolk-shelled ZnCo<sub>2</sub>O<sub>4</sub> sensor was highly sensitive to detect ozone gas down to 80 ppb with both *a.c.* and *d.c.* electrical measurements, with fast response and recovery, and good selectivity. The mechanism of detection was found to be based on adsorption of ozone molecules on the ZnCo<sub>2</sub>O<sub>4</sub> surface, as a layer of holes is created which affects the conductivity, as in a typical p-type semiconductor. Finally, the enhanced performance owing to the large surface area to volume ratio of ZnCo<sub>2</sub>O<sub>4</sub> yolk-shelled microspheres is promising for developing further gas sensor devices to monitor the environment.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.snb.2017.11.041>.



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- Oswaldo N. Oliveira Jr.** is a physics professor at the São Carlos Institute of Physics, University of São Paulo, Brazil. He has led research into the fabrication of novel materials in the form of ultrathin films obtained with the Langmuir–Blodgett and self-assembly techniques. Most of this work has been associated with fundamental properties of ultrathin films with molecular control, but technological aspects have also been addressed in specific projects. This is the case of an electronic tongue, whose response to a number of tastants is considerably more sensitive than the human gustatory system and the use of chitosan nanostructured films for covering textiles. In recent years, Prof. Oliveira has pioneered the combined use of methods from distinct fields of science, with the merge of methods of statistical physics and computer science to process text, and use of information visualization to enhance the performance of sensing and biosensing. This pioneering work is associated with the merge of nanotechnology with Big Data Analytics, bound to yield developments in technology such as computer-aided diagnosis systems.

## Biographies

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