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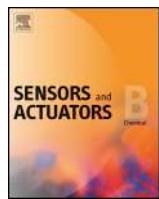
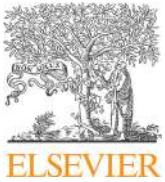
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Research Paper

Yolk-shelled ZnCo₂O₄ 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 μm yolk-shelled ZnCo₂O₄ microstructures synthesized via an eco-friendly, co-precipitation method and subsequent annealing. With these ZnCo₂O₄ 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 CO, NH₃ and NO₂. 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 ZnCo₂O₄ surface create a layer of holes that affect the conductivity, as in a p-type semiconductor. Since this mechanism of detection is generic, ZnCo₂O₄ 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 CO, NO₂ and NH₃ 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 (O₃) 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 uncapable to meet the requirement of detecting ozone at the ppb level [14]. There are exceptions though, including some n-type semiconductors, viz. ZnO [15], SnO₂ [16], WO₃ [17], α-AgWO₄ [18], NiCo₂O₄ [19] and In₂O₃ [20], especially the nanocrystalline In₂O₃ 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 (AB₂O₄) 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 (ZnCo_2O_4) used in Li-ion batteries [42] and as a hole transport layer in organic photovoltaics (PVs) [43]. Nanostructured ZnCo_2O_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 ZnCo_2O_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 ZnCo_2O_4 yolk-shell microspheres

The ZnCo_2O_4 compound was synthesized using the co-precipitation method [45], in which ZnCo_2O_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 min⁻¹ during 5 h, leading to crystalline ZnCo_2O_4 powder. The synthesis procedure of pristine ZnCo_2O_4 is schematically illustrated in Fig. S1 in the electronic Supplementary information.

2.2. Material characterization

The crystalline phase of ZnCo_2O_4 samples was identified by X-ray diffraction (XRD), using $\text{CuK}\alpha$ radiation (Rigaku, Rotaflex RU-200B) in the 2θ range from 10° to 80° with a step of 0.02° and step scanning of 2° min⁻¹. The morphological characteristics of ZnCo_2O_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 ZnCo_2O_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 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 $\text{Al K}\alpha$ 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 ±0.1 eV.

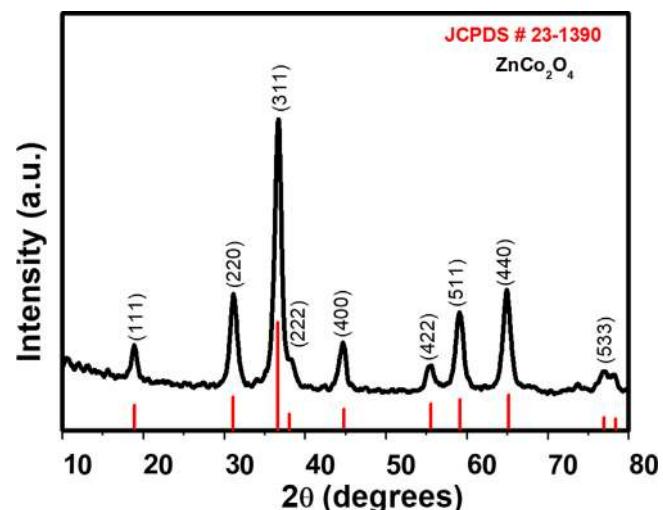


Fig. 1. XRD pattern of ZnCo_2O_4 annealed at 350 °C for 5 h in ambient atmosphere.

2.3. Fabrication of ZnCo_2O_4 sensing film and gas-sensing measurements

Gas sensing devices were fabricated by ultrasonically dispersing the as-prepared ZnCo_2O_4 powders (10 mg) in 1 mL isopropyl alcohol and the suspension was then drop-cast onto a SiO_2/Si substrate containing 100 nm thick Pt electrodes separated by a distance of 50 μm . Details of preparation of the interdigitated electrodes (IDEs) are given in [19]. After dropping the ZnCo_2O_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 (NO_2), carbon monoxide (CO) and ammonia (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):

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

where $\Delta R = R_g - R_d$ for oxidizing gases like ozone, and R_g and R_d 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 ZnCo_2O_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.

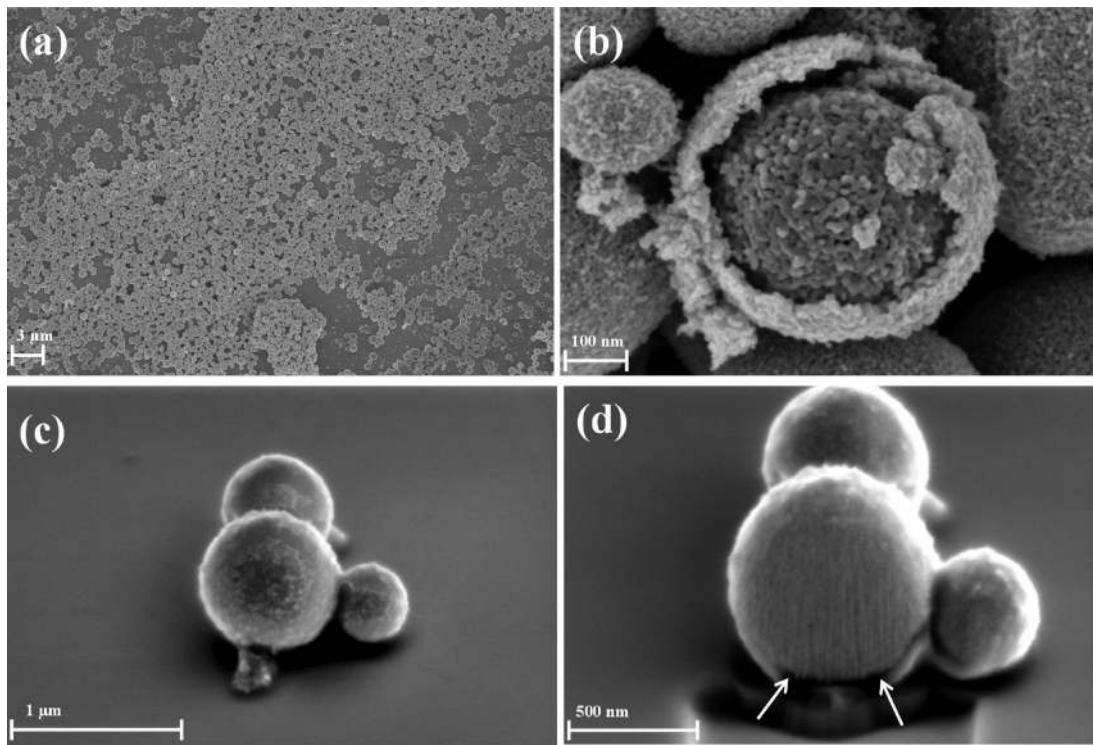


Fig. 2. (a and b) FE-SEM images with different magnifications of ZnCo_2O_4 annealed at 350°C for 5 h. (c) As deposited and (d) FIB-sectioned ZnCo_2O_4 sample displaying the yolk and the shell parts.

3. Results and discussion

3.1. Structural and microstructural characterizations

ZnCo_2O_4 yolk-shelled microspheres were synthesized via an eco-friendly precipitation route without any surfactant. Fig. S3 shows the thermogravimetric analysis (TGA) curve of ZnCo-glycolate precursor which indicates a total weight loss of 45.5% above 300°C . Two major weight loss steps were identified: the first loss of $\sim 12\%$ up to 210°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 ZnCo-glycolate into ZnCo_2O_4 . Above 300°C no weight loss was observed, which confirms the formation of pure ZnCo_2O_4 phase. To ensure complete decomposition of the precursor, we chose 350°C as the calcination temperature for the synthesis of ZnCo_2O_4 .

Fig. 1 displays the XRD pattern of ZnCO_2O_4 powder annealed for 5 h at 350°C , where all reflections were indexed to a face-centered-cubic (fcc) arrangement with $\text{Fd}3\text{m}$ (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 N_2 adsorption–desorption isotherms for the yolk-shelled ZnCo_2O_4 in Fig. S4 is classified as type III, with a type 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 ZnCo_2O_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, ZnCo-glycolate is formed due to interlinking of ethylene glycol at 170°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 ZnCo-glycolate under non-equilibrium conditions. As the temperature reaches 350°C during calcination, the ZnCo-glycolate core starts to decompose into ZnCo_2O_4 , thus eventually leading to a ZnCo_2O_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 ZnCo_2O_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°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 ZnCo_2O_4 phase, consis-

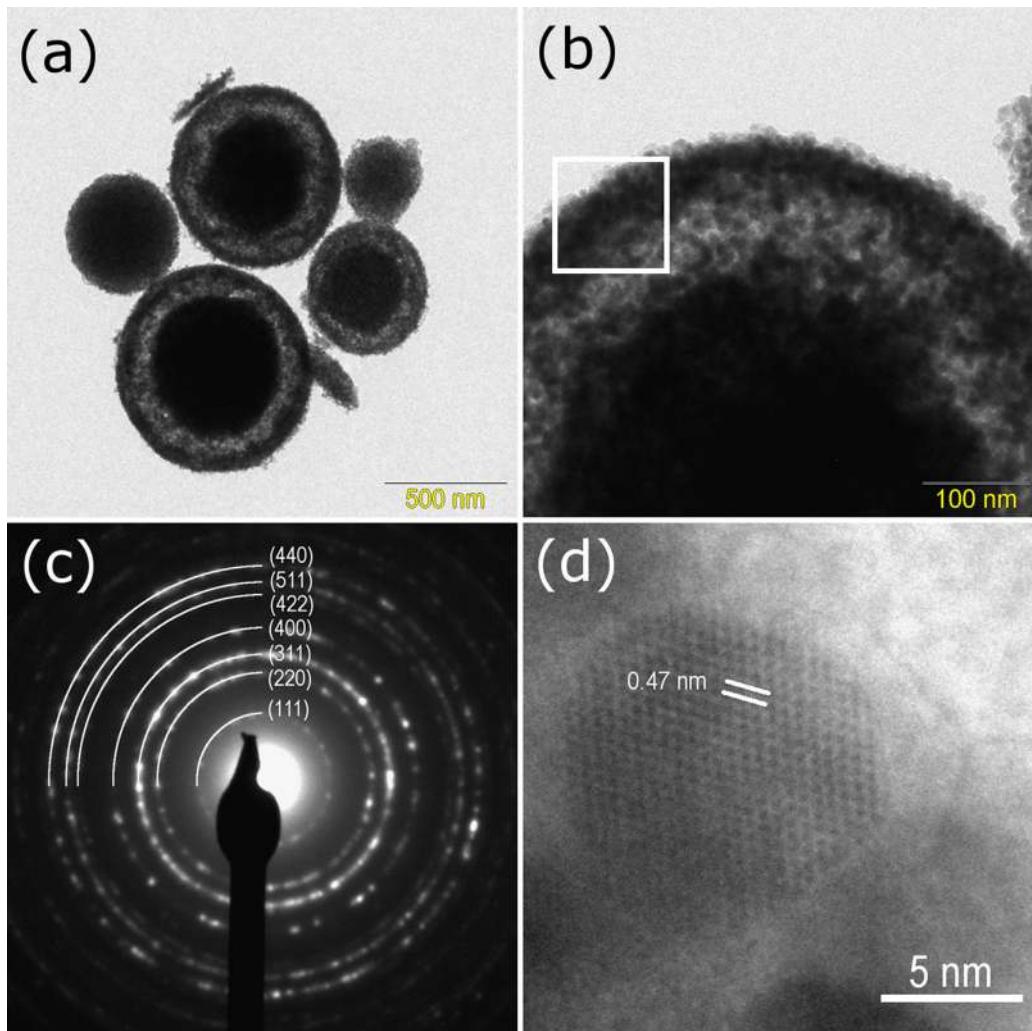


Fig. 3. (a and b) Low and high magnification TEM images of the yolk-shelled ZnCo_2O_4 microspheres. (c) SAED pattern (d) HRTEM image at the edge of a microsphere.

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 ZnCo_2O_4 phase.

The chemical elements comprising the ZnCo_2O_4 yolk-shelled 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 Zn^{2+} with the orbits of Zn 2p_{3/2} and Zn 2p_{1/2}, 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_{3/2} and Co 2p_{1/2}, respectively, with spin-orbit splitting of around 15 eV owing to mixed Co^{2+} and 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 ZnCo_2O_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 ZnCo_2O_4 yolk-shelled 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 ZnCo_2O_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

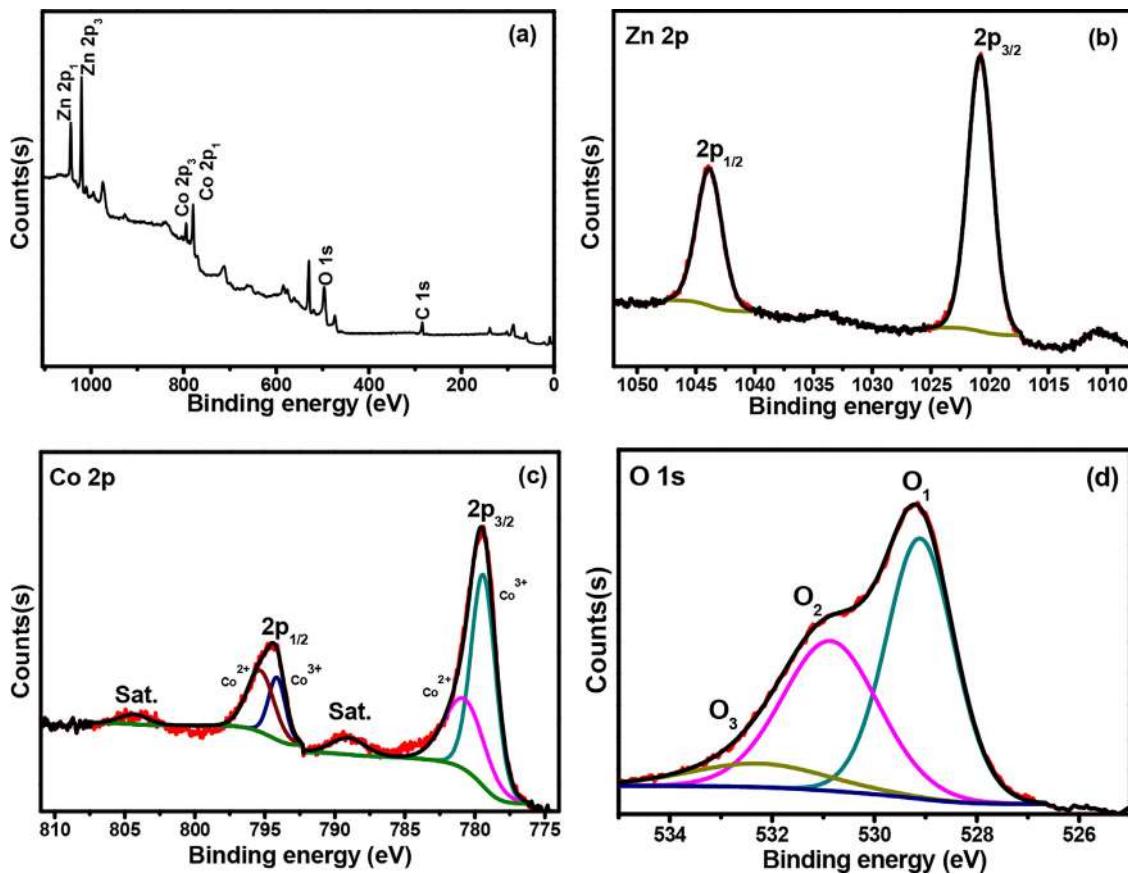


Fig. 4. XPS spectra of the ZnCo_2O_4 structure. (a) Survey scan and high resolution scan of (b) Zn 2p, (c) Co 2p, and (d) O 1s regions.

Table 1
Ozone gas sensing parameters for ZnCo_2O_4 microspheres at 200°C .

O ₃ 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 ZnCo_2O_4 yolk-shell 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 ZnCo_2O_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 ZnCo_2O_4 yolk-shell microspheres exposed to 1 ppm of reducing (CO and NH₃) and oxidizing (O₃ and NO₂) 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 O₃ (~71%) than for NO₂ (6.5%), NH₃ (3.8%) and CO (4.8%). Therefore, the ZnCo_2O_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 ZnCo_2O_4 yolk-shell microspheres

The ZnCo_2O_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 $0.912 \times 10^{-10} \text{ F}$, 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

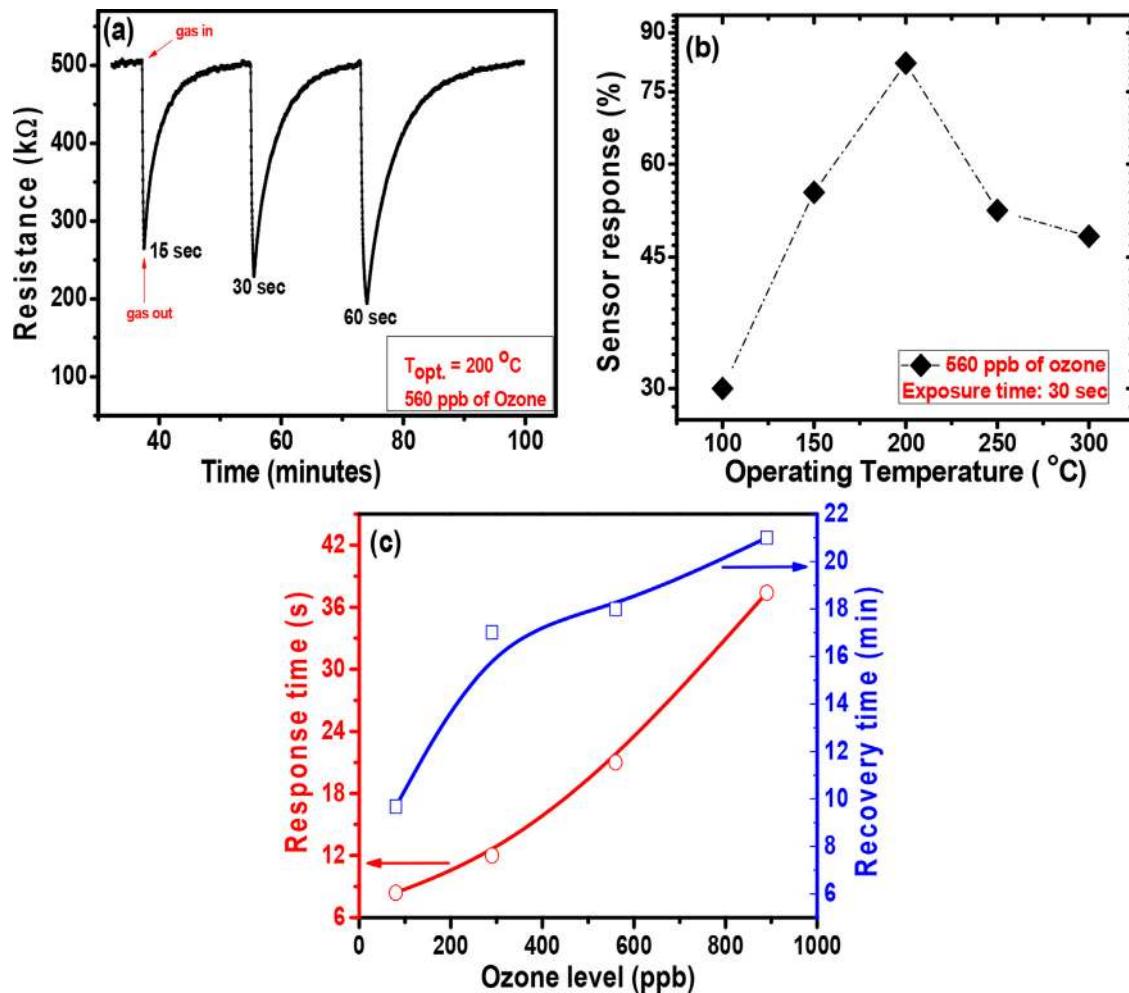


Fig. 5. (a) Dynamic electrical resistance of ZnCo_2O_4 sample exposed for different periods of time to 560 ppb of O_3 at 200°C . (b) Sensor response of the ZnCo_2O_4 sample exposed to 560 ppb O_3 at different operating temperatures. (c) Response and recovery time as a function of ozone concentration from 80 to 890 ppb at 200°C .

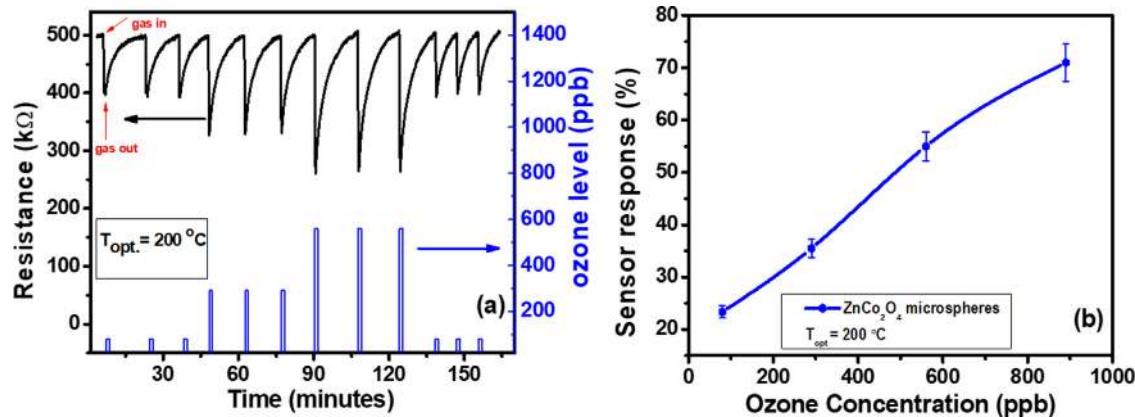


Fig. 6. (a) Dynamic electrical response of ZnCo_2O_4 sample of three cycles for each ozone concentration (b) Sensor response vs ozone concentration in the range of 80–890 ppb for ZnCo_2O_4 microspheres at 200°C .

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

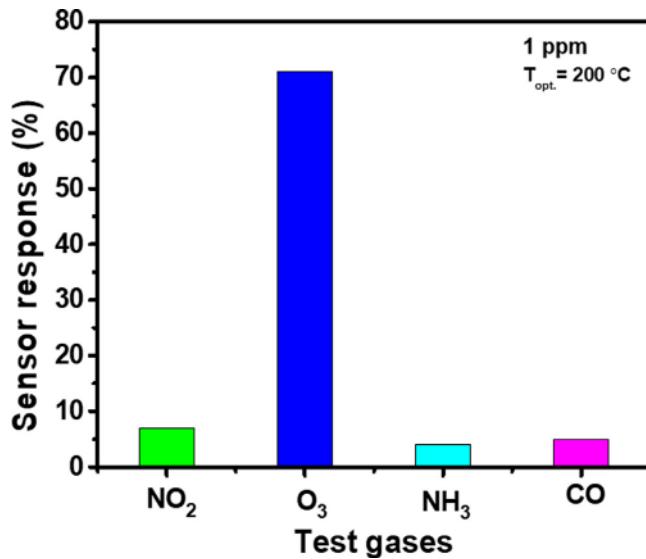


Fig. 7. Selectivity histogram of the ZnCo₂O₄ yolk-shell microspheres exposed to common gases present in the atmosphere.

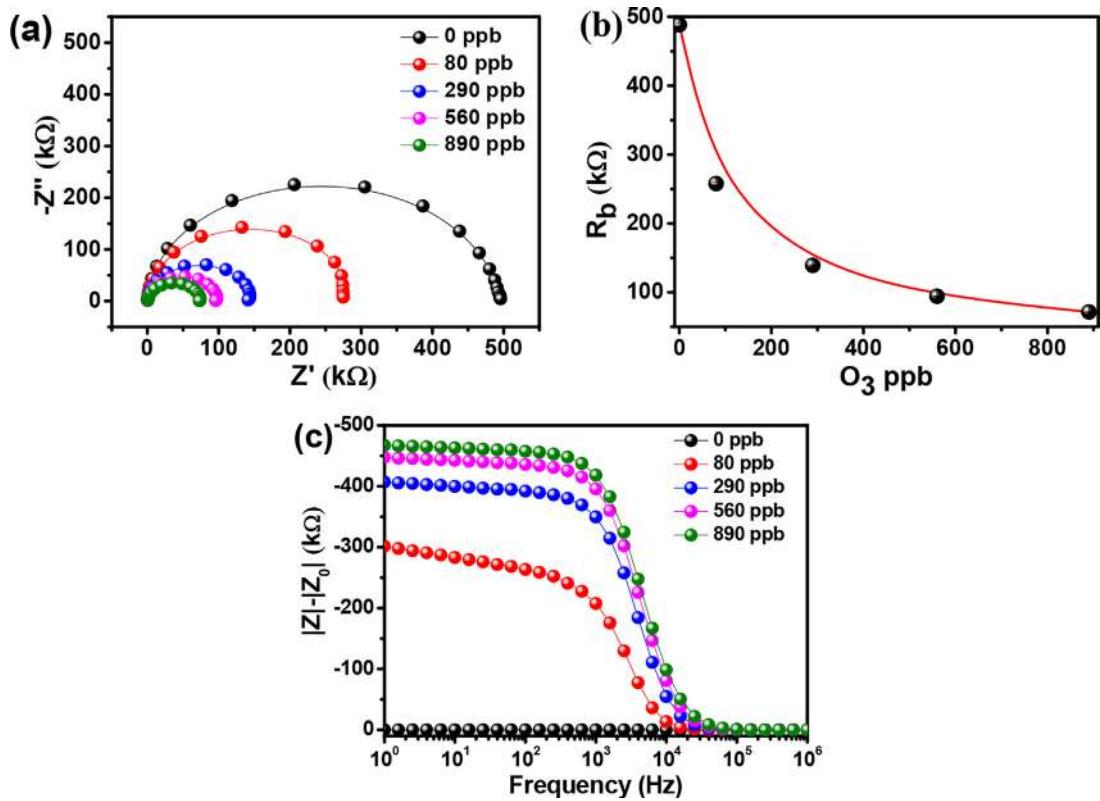


Fig. 8. (a) Nyquist plot of ZnCo₂O₄ film in air and after ozone exposure at 200 °C. (b) R_b values from fitting with an equivalent circuit as a function of ozone concentration. (c) Relative magnitude impedance spectra of ZnCo₂O₄ sample at 200 °C from 1 Hz to 1 MHz for different ozone concentrations.

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 μF 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

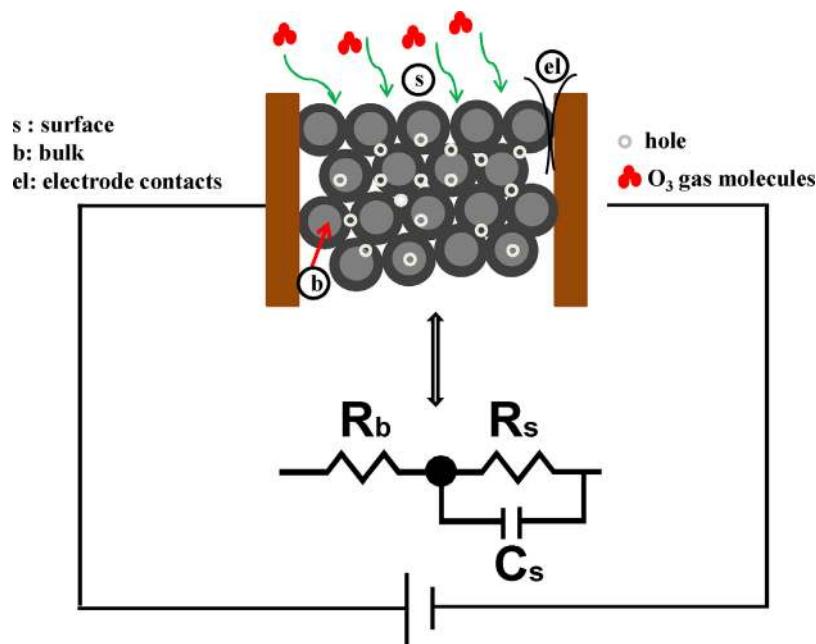


Fig. 9. Schematic representation of the gas sensing material and electrical equivalent circuit to fit the impedance data.

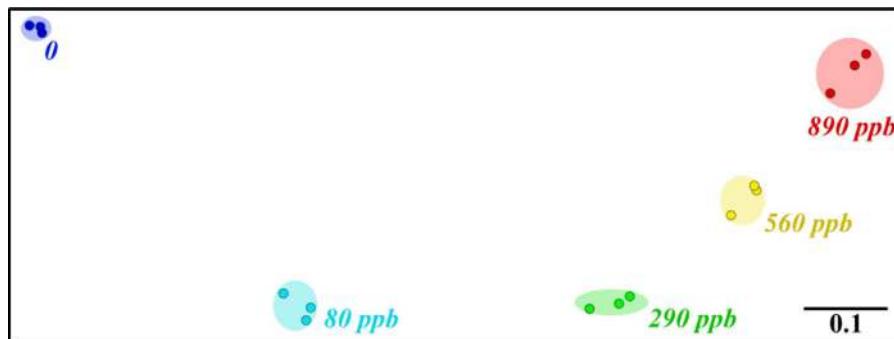


Fig. 10. IDMAP plot of normalized magnitude impedance spectra for different ozone gas concentrations. The scale bar represents the Euclidean distance of 0.1.

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 ₃ (ppb)	R _b (Ω)	R _s (k Ω)	C _s (pF)
0	458.4 \pm 37.1	488.7 \pm 3.0	90.7 \pm 0.7
80	427.5 \pm 62.2	258.4 \pm 2.6	90.7 \pm 1.2
290	442.9 \pm 30.2	139.6 \pm 0.6	91.0 \pm 0.6
560	447.2 \pm 26.5	94.7 \pm 0.4	91.5 \pm 0.6
890	455.7 \pm 24.6	71.9 \pm 0.3	92.0 \pm 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 ZnCo₂O₄ 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 ZnCo₂O₄ microspheres can be synthesized by co-precipitation and subsequent annealing. The structure, morphology and composition of the ZnCo₂O₄ were confirmed with

several methods, namely XRD, FE-SEM, TEM and XPS. The yolk-shelled ZnCo₂O₄ 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 ZnCo₂O₄ 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 ZnCo₂O₄ 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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