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# Pt-decorated $In_2O_3$ nanoparticles and their ability as a highly sensitive (<10 ppb) acetone sensor for biomedical applications

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ABSTRACT

This paper reports on the high sensitivity of sub-spherical $In_2O_3$-Pt nanoparticles (NPs) for detecting ppb levels of acetone, a biomarker for diabetes. The $In_2O_3$-Pt NPs, in the form of monodisperse metal-oxide $In_2O_3$ NPs with diameters of 6–8 nm, decorated with 2 wt% Pt metal NPs (2–3 nm) on the surface, were synthesized by a novel non-aqueous sol–gel route. NPs samples were investigated by X-ray powder diffraction (XRPD), using the advanced whole powder pattern modeling (WPPM) method, and high-resolution transmission electron microscopy (HR-TEM). The advantage of this preparative process is that it preserves metallic platinum NPs formed during the synthesis. The highly sensitive acetone sensor based on these NPs, showed a lower detection limit as low as 10 ppb or less, which is the lowest detection limit ever reported for any chemoresistive acetone sensors. This exceptional performance is likely due to the key role played by very small Pt metal NPs uniformly distributed in the $In_2O_3$-Pt nanostructure. The developed sensor would be suitable for use as a highly sensitive, practical breath acetone checker for daily diet and diabetes management and diagnosis.



## 1. Introduction

The synthesis of metal oxide nanoparticles (NPs) is one of the most exciting and extensively studied research field in recent years, due to the peculiar properties of these nanomaterials which make them highly suitable for different applications in optical, electrical and optoelectronic devices, catalysis, chemical sensors, and so on [1–3]. In particular, metal oxide nanoparticles, including ZnO, $V_2O_4$, $SnO_2$, $WO_3$, $Fe_2O_3$, $In_2O_3$, etc., have been demonstrated to operate very well as sensitive elements in resistive sensors for detecting many gaseous substances such $NO_x$, CO, ozone, $CH_4$, ethanol, etc [4,5].

Many factors can influence the performances of these nanomaterials, such as synthesis methods, size and shape of crystalline NPs, crystallinity degree, porosity and especially the presence of metal dopants [6].

Among these, Pt-decorated $In_2O_3$ NPs, have recently attracted attention for their improved gas sensing properties for CO, $H_2$ and $C_2H_5OH$, compared to undoped/pure $In_2O_3$ metal oxide NPs [7]. Great efforts have been put in by Neri's group to investigate the gas sensing of Pt-doped $In_2O_3$ NPs, aimed to the development of innovative and low cost devices capable of real time and fast detection of gaseous species [8–11].

There are several procedures to synthesize $In_2O_3$ NPs and core–shell Pt@$In_2O_3$ NPs, including hydrothermal methods [5], flame spray pyrolysis [12], electrodeposition [13], non-hydrolytic alcoholysis [14] and microwave-assisted synthesis [15]. Most methods are carried out in the presence of toxic organic solvents and surfactants, the reaction parameters also involving high temperature and long reaction times. These synthesis procedures are often limited, and it is difficult to accurately control the reaction parameters.

For industrial applications, the development of feasible synthetic processes is of paramount importance, and it is really

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important to develop a straightforward process for producing $In_2O_3$ and Pt@$In_2O_3$ nanoparticles for the above applications. To this end, a facile/scalable method to produce $In_2O_3$ NPs via a one-pot non-aqueous sol–gel route at low-temperatures has been developed. In our previous work, we have developed a novel and facile non-aqueous sol–gel route for producing pure $In_2O_3$ metal oxide NPs. In the present study, we further develop this advanced methodology to prepare, easily and at relatively low cost, $In_2O_3$-Pt (2 wt%) metal/metal-oxide nanoparticles, in which the larger oxide NPs are decorated with much smaller metallic NPs on their surface. Detailed studies, including synthesis formation mechanism, structural and physico-chemical characterization, and application of the $In_2O_3$ NPs as a resistive gas sensor for sevoflurane anesthetic, are available in our previous work [16]. In this current paper, the hybrid $In_2O_3$-Pt (2 wt%) NPs were tested for the gas sensing detection of acetone in human breath.

Human breath analysis is rapidly gaining ground as a means to noninvasively diagnose and monitor various aspects of metabolism linked to several diseases [17]. This is possible because there is an almost instantaneous equilibrium between the pulmonary blood and the air in the alveoli of the lung. Several breath components are known to be related to specific human diseases: acetone for diabetes [18] ammonia for diseases in amino acids metabolism [19], hydrogen for lactose intolerance [20], etc.

In spite of the potential, breath analysis has not found systematic applications in routine biological monitoring for diagnostic purposes, since the analytical procedures described in literature could hardly be used for routine analysis. Indeed, laboratory analysis of exhaled air is a complex, expensive and time consuming process, using GC–MS analysis to detect specific compounds, and thus is not in wide spread use. Sensor-based electronic devices are gaining the main role when specific disease markers have been defined for a new generation of breath test instruments that could, in time, become as ordinary and versatile in medical screening as blood tests are today.

Among these biomarkers, acetone is found in anomalous concentration (threshold limit 1.7 ppm) in breath samples of peoples with diabetes [21]. The detection of very low concentrations of acetone detection using chemoresistive sensors ($MO_x$ sensors) has been widely investigated [22–30]. Among the most sensitive so far reported, flame-made Cr-doped $\varepsilon$-$WO_3$ nanoparticles display a response to low concentration of acetone as low 200 ppb [27]. $In_2O_3$ hollow microspheres prepared by a hydrothermal and subsequent annealing process are reported to offer good response with low detection of <500 ppb [28]. Recently, it has been demonstrated that Au/$In_2O_3$ nanorods can effectively detect acetone with a low detection limit as low as 100 ppb [30]. Here, we report a study focused on the development of Pt-doped $In_2O_3$ nanoparticles as sensing materials for detection of ultra-low concentration of acetone. Results showed that a highly sensitive acetone sensor, based on $In_2O_3$-Pt (2 wt%), was developed, showing an extremely low detection limit of 10 ppb or less, which is the lowest detection limit ever reported for acetone chemoresistive sensors, making this an unprecedented result in the literature.

## 2. Experimental

### 2.1. Chemicals and materials

Indium(III) acetylacetonate [$In(OCCH_3CHOCCH_3)_3$] (≥99.99%) trace metals basis, platinum(II) acetylacetonate [$Pt(C_5H_7O_2)_2$] (≥99.99%) trace metals basis and butylamine (99.5%) [$CH_3(CH_2)_3NH_2$] were used, all from Aldrich.

### 2.2. Synthesis of $In_2O_3$ nanoparticles and Pt (2 wt%) doped $In_2O_3$

The synthesis was carried out in a glove box ($O_2$ and $H_2O$ < 1 ppm). In a typical procedure, 1 mmol (0.5 g) of Indium(III) acetylacetonate [$In(OCCH_3CHOCCH_3)_3$] were added to 15 mL of *n*-butylamine, the reaction mixture was transferred into a stainless steel autoclave, and carefully sealed. The autoclave was taken out of the glove-box and heated in a furnace at temperatures at 140 °C for 4 h. In the case of the Pt-doped nanoparticles, 2 wt% (the synthesis time was only 4 h) indium(III) acetylacetonate was replaced by anhydrous platinum acetylacetonate. The resulting milky suspensions were centrifuged, and the precipitates were thoroughly washed with ethanol and dichloromethane, and dried in air at 60 °C.

### 2.3. Sample characterization

A semi-quantitative phase analysis (QPA) of the crystalline phases in the prepared samples was obtained by X-ray powder diffraction (XRPD) using the Rietveld method, as implemented in the GSAS software with its graphical interface EXPGUI [31,32]. Data were collected on a PANalytical X'Pert Pro (NL) $\theta/2\theta$ diffractometer equipped with 0.5° divergence slit, 0.5° anti-scattering slit, 0.04 rad Soller slits, and a 15 mm copper mask in the incident beam pathway and a fast RTMS detector (PIXcel 1D, PANalytical) on the diffracted arm.

The XRPD data were collected in the 14–115° $2\theta$ range using Cu Kα radiation (45 kV and 40 mA) with a virtual step scan of 0.02° $2\theta$ and virtual time per step of 500 s. The starting atomic parameters for $In_2O_3$ described in the SG $Ia\bar{3}$ were taken from a previous work of the present authors [16]; those for InO(OH), SG Pnnm, from Christensen et al. [33]. The refined parameters were: scale-factors, zero-point, six coefficients of the Chebyshev background polynomial, unit cell parameters, two Lorentzian ($L_X$ and $L_Y$) terms, and one angle independent Gaussian term ($G_W$) as the profile coefficients, and sample displacement effects. Microstructural analysis was exploited via XRPD as well, using the same data as those for the QPA analysis, and employing the whole powder pattern modeling (WPPM) [34,35] implemented in the PM2K software [36]. This novel technique, considered a state-of-the-art, describes each observed peak profile as a convolution of instrumental and sample-related physical effects, refining the corresponding model parameters directly on the observed data [37,38]. The instrumental contribution was obtained by modeling 14 hkl reflections from the NIST SRM 660b standard ($LaB_6$), according to the Caglioti et al. relationship [39]. Afterward, $In_2O_3$ (SG $Ia\bar{3}$), and where present InO(OH) (SG Pnnm), were included in the WPPM modeling. The following parameters were refined: background (modelled using a 4th-order of the shifted Chebyshev polynomial function), peak intensities, sample displacement, and lattice parameters; crystalline domains were assumed to be spherical, and distributed according to a log-normal size distribution.

Transmission electron microscopy (TEM) was performed using a Jeol-2000 FXII microscope, with point-to-point and line-to-line resolutions of 0.28 nm and 0.14 nm, respectively. High resolution TEM (HR-TEM) was performed using a JEOL 2200FS microscope with a field emission gun, operated at 200 kV. Samples for TEM/HR-TEM observations were prepared by dispersing the NPs in ethanol and evaporating the suspension drops on carbon-coated copper grids.

### 2.4. Sensing tests

The sensing device consists of an alumina substrate ($6 \times 3\ mm^2$) with Pt interdigitated electrodes and a Pt heater located on the backside, on which the sensing layer (1–10 μm thick) was deposited by screen printing. A multimeter data acquisition unit Agilent 34970A was used for this purpose, while a dual-channel