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Highlights

- A tunable loading of Au NPs with uniform dimension is efficiently deposited directly on the surface of MWCNTs-based sensor device by an electrophoretic process.
- Au-decorated MWCNTs-based gas sensors have a higher thermal stability than pristine.
- A fine tune of Au loading on MWCNT-based gas sensors permits to control the sensitivity and selectivity towards a specific gaseous analyte.

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Electrophoretic deposition of Au NPs on MWCNT-based gas sensor for tailored gas detection with enhanced sensing properties

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Abstract

Multiwalled carbon nanotube (MWCNT)-based gas sensors were decorated by an electrophoretic deposition of electrochemically preformed gold nanoparticles (Au NPs) with controlled size and loading, for the detection of gaseous pollutants at sub-ppm concentrations and operating temperature in the range of 100–200°C. The effects of the tailored Au content on the sensitivity and selectivity of MWCNT-based gas sensors were evaluated towards the NO₂ monitoring, and also towards some interfering reducing gases, such as NH₃ and H₂S. Gas sensing measurement revealed the highest NO₂ response up to sub-ppm level by using MWCNTs functionalized by the lowest Au content; instead, the worse NO₂ response was obtained by modified MWNTs containing the highest Au loading. Moreover, the control of the deposited gold loading has allowed to control the MWCNT sensing response; specifically the increase of gold content on MWCNT has reduced the selectivity and sensitivity towards NO₂ gas, and, on the contrary, at the same time it has improved those towards H₂S and NH₃ interfering gases. Finally, binary gas mixtures (NO₂/H₂S and NO₂/NH₃)

were performed to evaluate the detection of the targeted NO₂ gas, simulating possible real-world conditions.

Keywords: Au NPs, MWCNTs networks, CNT-based gas sensor, binary mixtures, electrophoresis.

1. Introduction

The detection of chemical gaseous species in the atmosphere is of great interest concerning the environmental pollution, industrial and traffic emission monitoring, process control, and public security [1]. The development of portable gas sensors able to detect toxic and hazardous gases in real time with good sensing performance will significantly improve the air-pollution control and the environmental sustainability [2, 3]. Among various nanomaterials, carbon nanotubes (CNTs) hold great promise for the development of miniaturized sensors with high sensitivity, low-power consumption and low-cost [4-6]. Their superior sensing performance depends on: (1) a high adsorption capacity given by the large surface-area-to-volume ratio [7], (2) a good modulation of electrical properties (e.g. capacitance, resistance) upon exposure to gaseous analytes due to a greater interaction zone (i.e. Debye length) over the cross-sectional area [8], (3) the ability to tune electrical properties of the nanostructure by adjusting the composition and size [9], and (4) the ease of configuration as chemiresistors and potential integration with low-power microelectronics to form complete systems with microprocessor and wireless communication units [10].

CNT-based chemiresistive gas sensors are able to detect very low concentrations of gaseous molecules with high sensitivity under ambient conditions [11, 12]; specifically, semiconducting CNTs are extremely sensitive to charge transfer and chemical doping effects by various molecules: In presence of electron-withdrawing molecules (e.g. NO₂, O₃, O₂) or electron-donating molecules (e.g. CO, H₂S, NH₃), semiconducting CNTs interact as a *p-type* semiconductor, changing the density of the main charge carriers (holes) in the nanotube, which changes the conductance of CNTs [11, 10]. Moreover, M. Meyyappan *et al.* [13] have suggested sensing mechanisms such as

intratube modulation and *intertube modulation*, based on electron hopping in the individual nanotubes and their networks, respectively, through molecule adsorption into single-walled carbon nanotubes.

Recently, the electrical transport in individual SWCNT field-effect transistors has been reported for gas sensing applications at room temperature with ultra-low power consumption [14].

However, since their strong sp^2 bonding and near-perfect hexagonal network, pristine CNTs are characterized by a low chemical reactivity with the molecular environment, thus preventing the formation of strong chemical bonds with most molecules; therefore, their sensing response is weak and scarcely selective, irreversible with long recovery time [15]. To overcome these drawbacks several groups have focused their research to improve the response of sensors based on CNTs networks without any chemical functionalization [13], but simply by increasing the operation temperature [16], by subjecting the device to centrifugal force [17], or by varying sensor architectures [18]. Beside these strategies, another approach consists in the functionalization of CNTs sidewalls with suitable materials, including hybrid functional structures [19], polymers, metal oxides and metals. This method has been already demonstrated to enhance the sensing capability of CNTs by improving their reactivity and sensitivity; therefore, many covalent and non-covalent methods have been employed to functionalize CNTs with various materials, which modify the CNT-surface reactivity, improving the gas detection [20]. Alternatively, metal nanoparticles (NPs) can be used to decorate CNTs, creating hybrid nanocomposite materials with improved sensing performance, leading to enhanced sensitivity, faster response/recovery, and better selectivity in CNT-based gas sensors [21]. Theoretical and experimental investigations reveal that metal NPs are an integral active part of the sensor, whose detection capability is mainly based on its surface reactivity [21]. Specifically, studies have indicated that the transition metal has a rich d-electron and empty orbit, and the small gas molecule can bond strongly to the metal when adsorbed on the surface [22]. Among metal nanophases, gold (Au) NPs have a high sensitivity, good electrical conductivity and excellent catalytic activity [23, 24], that can be tuned by controlling the particle

size and the architecture of the metal-support interaction [25]. Moreover, gold nanostructures, assembled with various methods, have been intensively investigated not only as sensitizers for other materials but also as independent building blocks to fabricate gas sensors [26], especially to detect H₂S [27, 28], depending on the good chemical affinity between S and Au atoms [29, 30], and to monitor NO_x [31]. Therefore, the modification of CNT-based gas sensors using gold nanoparticles to improve their sensing performance has become a quite popular research topic. Lee *et al.* [32] have reported the detection at room temperature of 255 ppb of NH₃, that is one of the lowest values of concentration detected, using Au modified CNTs films. Mubeen *et al.* [33] have reported Au nanoparticle-modified single-walled carbon nanotube-based gas sensor with a good sensitivity, rapid response and recovery time toward H₂S at room temperature, detecting up to 2 ppb, and also an excellent selectivity toward CO and SO₂ with minimum interference from NH₃. Penza *et al.* [34] have reported a significant improvement of NO₂ sensitivity for Au-functionalized multi-walled nanotubes randomly arranged. Therefore, the more relevant gas sensing responses reported in literature regarding the use of Au-decorated MWCNTs as gas sensor to monitor the major pollutant gases are summarized in Table 1. Based on these results, it was shown that the sensitivity of the CNT gas sensor depends not only on the sensor working temperature but also on Au NPs [39], since the nanoscale size of the metal cluster maximizes the effect of the gas adsorption and so affects the electron transport in the CNTs by charge transfer. Moreover, considering the nature of metal NPs, it has been demonstrated that gold is inert in bulk form but it is catalytically active in the nanometer range [40]; its increased reactivity is due to the presence of low-coordinated gold atoms on the corners and edges of particles, particularly abundant on the nanometer-sized particles [24]. Indeed, Au NPs loading has been reported to strongly influence CNT sensor sensitivity [34].

Until now, different approaches have been used in order to deposit Au NPs on the top of the MWCNT networked films, such as thermal evaporation [41], sputtering [34], and electrochemical deposition [42], although some of their limits are the uncontrolled clustering formation at high

metal loading that negatively affects catalytic properties of metal nanoparticles, and a possible damage of CNTs structure.

In this work, we propose an alternative method to directly functionalize MWCNT-based gas sensors with Au NPs; the process consists in an electrophoretic deposition of electrochemically pre-synthesized colloidal Au NPs with defined nano-size dimension. The proposed functionalization process permits to control the quantity of deposited Au NPs by tuning the time of the electrophoresis, avoiding the clustering of Au NPs; therefore, only the influence of gold loading on the gas sensing performance of MWCNT-based gas sensors has been evaluated.

The morphology of the nanostructured active layers and their chemical composition were characterized by using Scanning and Transmission Electron Microscopies (SEM and TEM), and X-ray photoelectron spectroscopy (XPS), respectively.

The sensing performance of pristine and Au-modified MWCNT-based gas sensors towards the NO₂ gas and such common interfering reducing gases, as NH₃ and H₂S, was evaluated at different gas concentrations and at working temperatures in the range 100-200°C. The best response towards NO₂ gas was obtained by MWCNT-based gas sensor containing the lowest Au loading, detecting up to 0.1 ppm at an operating temperature of 150°C. On the contrary, a worsening of the responses towards NO₂ gas was revealed in MWCNT films with increased content of deposited Au; specifically, those films containing the highest Au loading showed the best response towards the interfering H₂S gas, detecting up to 0.1 ppm at a sensor temperature of 150°C. Therefore, the total surface amount of deposited Au NP has been demonstrated to control the CNT sensing capabilities. Specifically, a low Au NPs content improves the sensitivity towards NO₂ gas; instead, an high Au NPs content improves the sensitivity towards H₂S gas. The sensing properties have been controlled by the surface chemical composition: the decrease of XPS percentage ratio between the O1s content respect that of Au4f causes a decrease of NO₂ sensitivity and, on the contrary, an increase of that towards H₂S gas.

Finally, binary gas mixtures consisting of a fixed concentration level of a reducing gas (H_2S and NH_3) and various concentrations of the targeted oxidizing gas of NO_2 were investigated to evaluate the effects of the reducing interfering gases (H_2S or NH_3) on detection of the oxidizing NO_2 gas, in a real-world binary mixture.

2. Materials and methods

2.1. Preparation of Au modified MWCNT-based gas sensors

The colloidal solution containing Au NPs, used to directly decorate MWCNT-based gas sensors, was prepared by the sacrificial anode electrolysis (SAE), as described elsewhere [43]. The electrochemically synthesized Au NPs have a uniform dispersion with diameter of $12 \text{ nm} \pm 2 \text{ nm}$, as reported in TEM image in Figure 1 A. The net surface positive charge of Au NPs, given by the tetraoctylammonium (TOAC) surfactant [44-46], was used for the electrophoretic deposition to decorate the surface of MWCNTs; moreover, the anchorage of the colloidal Au NPs on the surface of MWCNT was guaranteed by the interaction between alkyl group of the surfactant and SWCNTs [47].

MWCNT networked films were grown by chemical vapor deposition (CVD) directly onto the alumina surface that was previously coated with a cobalt (Co) sputtered nano-sized catalyst of nominal thickness of 6 nm; substrates were then placed in a quartz boat and placed at the centre of a 1 inch diameter quartz tube reactor housed in a furnace [48]. Finally, a pair of metal strips of Cr/Au (20 nm/300 nm) was vacuum sputtered onto MWCNT films to serve as electrical contacts for the two-pole chemiresistor. The Cr/Au electrode sizes were 1 mm width \times 5 mm length, and the gap between the electrodes was 3 mm. In Figure 1 B, TEM image of MWCNTs is reported.

Modification of MWCNT-based devices was performed using an electrophoretic process based on a three electrodes cell in which a Pt wire was counter electrode, the CNT-based device was the working electrode and Ag/AgNO_3 (0.1 M in acetonitrile) was the reference electrode; the distance between the anode and the cathode was set at 2 cm. The electrolytic solution was the Au NP

colloidal solution (10 mM Au NPs and 5 mM TOAC in tetrahydrofuran and acetonitrile mixture in 3:1 ratio). The deposition process was cathodic: the applied working potential was a little bit more negative than the open circuit potential ($\eta = -200$ mV), so as to induce the migration of the colloidal Au NPs towards the negative cathode (CNT device), preventing the destroy of CNTs, and to reduce the residual gold ions in the positively charged shell [43], followed by its removal from the metal NPs surface, resulting in the SWCNTs surface decoration with Au NPs.

The excess of the surfactant from the functionalized device was completely removed by washing it with ACN for three times. The process was performed using three different deposition times, 90s, 300s and 600 s, resulting in different metal loadings. The scheme of the Au/SWCNT resistive gas sensor device is reported in Figure 2.

2.2. Material Characterization

The surface chemical characterization was performed by XPS, as a highly sensitive surface analysis method to detect the top 10 nm of film. A Thermo VG Theta Probe XPS spectrometer was used, equipped with a μ spot monochromatic Al K α source. The survey and the high-resolution spectra were acquired in fixed analyzer transmission mode with pass energies of 150 and 100 eV, respectively. Process reproducibility was checked by replicating selected experiments five times in different points selected in the device.

TEM images were obtained by means of a FEI TECNAI T12 transmission electron microscopy instrument.

The morphology of pristine and Au-decorated CNTs was analysed by SEM, using a Field Emission Zeiss Σ IGMA instrument at 5–10KV, 10 μ m aperture, directly on the sensor devices.

2.3. Setup for Gas Sensing Measurements

The CNT-based gas sensors were placed in a sealed stainless test cell (volume of 500 mL) for gas exposure measurements, as described in Ref. [34]. The cell was able to host up to 4 gas sensors

exposed simultaneously to the gas under test. The sensors were in thermal contact with a home-made heater sink, powered by a DC power supply system (Agilent 6644A, 0–60V/0–3.5 A), to control the desired set-point operating temperature. The DC electrical conductance of the CNT-based gas sensors was measured by the volt-amperometric technique in the two-pole format by a multimeter (Agilent, 34401A). The array of four chemiresistors were automatically scanned by a multiplexing switch system (Keithley, 7001) equipped by a low-current scanner card (Keithley, 7158). All data were acquired and stored for further analysis in a PC-based workstation, equipped with software compiled in Agilent-VEE. Dry air was used as reference and gas carrier, diluting the concentration of gaseous analyte, and to air-conditioning the sensors. The gas flow rate was controlled by distinct mass flow meters (MFC) with different full scales and controlled by G-MIX (Bioage) software. The total flow rate per exposure was kept constant at 1000 sccm. The gas sensing experiments were performed by measuring the resistance change of active layers in the two-pole format upon controlled ambient of NO₂ (0.1-10 ppm), NH₃ (5-1000 ppm), H₂S (0.1-10 ppm) individual gases. Binary gas mixtures were also programmed and controlled in term of ratio of gas flow rate at a fixed total rate as 1000 sccm and gas concentration for each component in the gas mixture. The sensing experiments were conducted at a sensor temperature in the range of 100–200°C to evaluate the temperature effect on gas sensing performance. The gas sensing cycle consisted of a period (at least 60 min) of stabilization of the sensor signals upon dry air (AirLiquide) flowing, an exposure time of 10 min to various targeted gas concentrations at increasing steps and finally a recovery time (at least 60 min) to restore the sensor signals with dry air flowing to clean the test cell and sensor surface. The sensor performance at a gas concentration was expressed as the normalized response defined as the ratio between the resistance change, ΔR , that is the change in resistance between the values of steady state of the electrical resistance, R_f and R_i , of the sensor upon a target gas and in air, respectively, and R_i in percentage; it can be calculate with Eq. (1)

$$\text{Norm. Response} = \frac{R_f - R_i}{R_i} * 100 (\%) \quad (1)$$

The mean gas sensitivity, S_m (% ppm⁻¹) is defined as weighted mean of the ratio between percentage relative resistance change (%) over gas concentration unit (ppm); it can be calculated with Eq. (2):

$$S_m = \frac{1}{n} \sum_{j=1}^n \frac{\left[\frac{\Delta R}{R_i} \right]_j}{c_j} \quad (\% \text{ ppm}^{-1}) \quad (2)$$

where c_j is a defined gas concentration to which corresponds the $[\Delta R/R_i]_j$ response.

The response time is defined as the time required for the variation in electrical resistance to reach 90% of the equilibrium value after injecting the gas; the recovery time is defined as the time needed for the sensor to return to 90% above the original resistance in air after removing the gas.

3. Results and discussion

3.1. Chemical and morphological characterization of gold-decorated MWCNTs

The surface chemical composition of pristine and of Au-decorated MWCNTs was evaluated by XPS. The detailed quantification of the chemical elements in the analyzed materials, reported in Table 2, showed that increasing the time of the electrophoretic process a higher quantity of Au was deposited on MWCNTs, as expected. Therefore, this result demonstrates that the deposited metal loading is controlled by the process time. Moreover, the atomic concentration of oxygen at the MWCNT surface increases from 5.0 to 7.8 at.% after gold deposition. The presence of oxygen is intrinsic to the CVD synthesis of MWCNTs and mainly arises from the oxygen adsorbed on their surface. The increase of the oxygen content after the MWCNT functionalization can be due to the generation of defects during the gold deposition [38, 49]. However, although the total oxygen

content in the MWCNT films increases together with the deposited Au content, at the same time, the XPS percentage ratio between the O1s content respect that of Au4f decreases. Finally, as it will be demonstrated further in the following section, the interactions at the interphase between the gaseous analyte and the sensing layer depend on the variation of this ratio with the gold content, so as to influence the sensing capability of modified MWCNTs.

The C1s spectra with fitting peaks of pristine and Au-functionalized MWCNTs are reported in Figure 3A a) and b), respectively. The C1s core level spectrum is the best monitor of the possible chemical changes onto the MWCNT surface after the electrochemical modification. The main component of C1s signal is at $283.7 \text{ eV} \pm 0.2 \text{ eV}$ is generated by sp^2 hybridized graphitic carbon atoms located on the walls of the MWCNTs and it is strongly asymmetric [50]; the peak at $284.8 \text{ eV} \pm 0.2 \text{ eV}$ is associated to photoelectrons emitted from amorphous carbon atoms with sp^3 bonds, formed during the MWCNTs synthesis as also detected by Raman spectroscopy [48, 51]; the peak at 290.4 eV corresponds to the electron energy loss peak due to π -plasmon excitations. These three peaks are characteristics of C1s core level from CNTs [52]. An additional peak at 286.4 eV is due to the presence of oxygenated carbon [53], and its atomic percentage corresponds to the oxygen percent in the film, demonstrating that the increase of oxygen content with the gold loading, as reported in Table 2, is caused by the generation of oxygenated defects on MWCNTs surface. Specifically, it has been demonstrated that the deposition of metal catalyst induces more defects on MWCNTs respect the pristine material, such as edges, dangling bonds, vacancies, dislocations, and steps. These defect sites are particularly reactive to oxygen, especially at high temperature [54].

The Au4f core level spectrum of MWCNTs decorated by the electrophoretic deposition of Au NPs is reported Figure 3 B. The signal is composed by a single doublet, attributed to Au in the elemental oxidation state. The position of the Au4f_{7/2} peak at $83.7 \text{ eV} \pm 0.2 \text{ eV}$ was a bit lower than that expected for bulk metallic Au at 84.0 eV [55], reasonably due to initial state size effects in small gold particles [56]. Therefore, the presence of gold nanoparticles demonstrate an effective functionalization of MWCNTs. Confirming these results, SEM images, reported in Figure 4,

display the morphology of pristine MWCNT networks and of those functionalized with Au NPs with controlled loading of 0.3, 0.5, and 1.1 at.%.

All SEM images reveal the characteristic tubular structure of MWCNTs networks, consisting of tangled nets of densely distributed chains. The average diameter of the carbon nanotubes seems to vary in the range of 10–30 nm. On the surface-functionalized MWCNTs, Au NPs partially decorate MWCNT sidewalls in non-continuous manner, with a higher density by increasing the metal content. Since the very small dimension of gold nanoparticles, to observe their size and shape on MWCNTs sidewalls TEM analysis was performed.

Based on TEM images reported in Figure 5, Au NPs exhibit a nearly spherical shape and a mean diameter of about 12 nm, keeping their initial structure and size, as reported in Figure 1 A.

The density of deposited Au NPs was mainly controlled by the duration of the electrophoresis with the given electrophoretic parameters.

The Au sensitization should strongly affect MWCNTs gas sensing properties, mainly sensitivity and selectivity; hence, the effect of Au NPs loading on MWCNT-based gas sensor performance is discussed in the next paragraph.

3.2. Gas sensing properties

Figure 6 reports the response, in terms of electrical resistance change (ΔR), of chemiresistors based on pristine and Au-decorated MWCNTs, exposed to the target NO_2 gas at two-times repeated concentrations (10 and 0.1 ppm), and, to evaluate the cross-sensitivity, to interfering reducing gases, specifically, NH_3 (1000 and 5 ppm) and H_2S (10 and 0.1 ppm), at a sensor temperature of 150°C . The electrical resistance of pristine and Au-functionalized MWCNT-based gas sensors decreases upon single gas exposure of the oxidizing gas (NO_2), and, instead, increases upon individual gas exposure of the reducing gases (NH_3 , H_2S) due to molecules adsorption. These results clearly demonstrate a *p-type* semiconducting behavior of the MWCNTs networked films, maintained also

after the functionalization with Au nanoclusters [39]. This *p-type* dominant character in the Au-modified MWCNT sensors is also confirmed in a previous work of the authors [57].

In order to study the effects of the operating temperature of the sensor on the gas sensing performance, the temperature was varied in the range of 100-200°C, as reported in Figure 7. In this specific case, the mean sensitivity of pristine and Au-decorated MWCNTs-based sensors toward NO₂ gas was reported at 100°C, 150°C, and 200°C. Although these results are related to NO₂, they can also be extended to the other gaseous analytes; in particular, the mean sensitivity of Au-decorated MWCNT films towards one of the tested gases (e.g., NO₂, H₂S, NH₃) is always higher than the un-modified MWCNT films, and for all gas sensors under test the maximum of mean sensitivity has been obtained at the intermediate temperature of 150°C. Usually, Au NPs are not very effective at high testing temperature, since they could agglomerate, decreasing, therefore, their catalytic properties with consequent decrease of the gas sensitivity; moreover, MWCNTs could decompose at higher temperatures. At low temperature, instead, the Au NPs/MWCNT sensors do not easily desorb the chemical gaseous species for a complete reversibility. Therefore, a mild heating at 150°C can help to desorb the species from the surface of the sensor active layer so that the baseline resistance could be fully recovered without loss of the catalytic effects in the Au NPs. This is not surprising because a rather strong interaction (chemisorption) between Au NPs decorated MWCNTs and gas, such as NO₂ and H₂S, has been reported [30, 31].

Moreover, operating at 150°C the baseline is restored at the resistance value before the gas exposition. To confirm this, in a recent paper although the sensing measurements towards NO₂ have been operated at room temperature, an heating period at 150°C has been used to clean the surface of CNTs after the exposure to NO₂ [58].

Considering the sensor operating temperature effect on sensing properties towards NO₂, as reported in Figure 7, the mean sensitivity of MWCNTs containing the lower Au loading (0.3 at.%) is always higher than that of the others, and the highest value has been obtained at operating temperatures of 150°C, although the maximum difference respect to the other values, in terms of mean sensitivity, is

obtained at 100°C. The same trend has been found towards NH₃; on the contrary, in presence of H₂S, the mean sensitivity of MWCNT networks with 1.1 at.% Au loading is the highest. The time responses for these gases was deeply investigated by individual gas exposures at decreasing concentration in a wider range by measuring the transient output signal of the electrical resistance change in the various chemiresistors. In Figure 8 the time responses towards NO₂, NH₃ and H₂S are reported using the four MWCNTs-chemiresistors without and with tuned loading of Au nanoclusters at a sensor temperature of 150°C. Excellent short-term repeatability of the response to the selected targeted gases has been measured for the Au-modified CNT-based sensors, as reported in Ref.[57].

The resistance variation, as expected, increases upon increasing the analyte gas concentration for all gas sensors, as reported in the calibration curves in Figure 9. In all plots, the trend of the sensor response to gas concentration is quite linear up to relative low gas concentrations, that is 1 ppm for NO₂ and H₂S, and 100 ppm for NH₃; above these values, at higher gas concentrations, the response variation is lower, probably due to the sensor saturation. Moreover, the responses to all the evaluated gaseous analytes at the operating sensor temperature of 150°C are higher for all Au modified MWCNTs compared to the pristine MWCNT film. In particular, the MWCNT sensor containing 0.3 at.% of Au shows the highest response towards the target NO₂ gas and the interfering NH₃ gas; instead, MWCNT networks containing the maximum content of Au NPs (1.1 at.%) exhibit the worse response to NO₂ and NH₃. On the contrary, the opposite trend is revealed in presence of H₂S; in this case, the MWCNTs with 1.1 at.% of Au NPs show the best response, instead, the CNTs networks containing 0.3 at.% of Au have the lowest response.

The better sensor responses towards all investigated gases at the operating temperature of 150°C are also accompanied by the faster sensor response for all Au-functionalized MWCNT-based gas sensor respect to pristine MWCNTs; specifically, the response time is reduced of about 2-3 min at all investigated concentrations in the range 10-0.1 ppm for NO₂ and H₂S and 1000-5 ppm for NH₃. On the contrary, no improvement of recovery process has been revealed. The presence of Au NPs on

the surface of MWCNTs improves the adsorption of gaseous molecules and the interaction at interphase, so that the response process is accelerated, but, at the same time, the strong interaction established limits the velocity of the recovery process.

The response time increases decreasing the gas concentration at all investigated operating temperatures; specifically, it is in the range of 1 min to 6 min under exposition to NO₂ (10-0.1 ppm) for MWCNTs containing the 0.3 at. % , and it increases increasing the gold content until the range of 2'-8'30'' for the MWCNTs containing the highest Au content. Therefore the content of deposited Au NPs on the surface of MWCNTs influences also the response time. The response is faster at the lowest Au content and decreases increasing the Au loading. This trend is explainable considering the same explanation given to the sensor response reported below.

Figure 10 compares the mean sensitivity of the four CNTs chemiresistors to NO₂, NH₃, and H₂S at the sensor temperature of 150°C. The gas sensing results demonstrate a significantly higher sensitivity of the Au-functionalized MWCNTs-sensors compared to the un-functionalized MWCNTs-devices according to a decreasing ranking for H₂S, NO₂ and NH₃. The gas sensitivity for a given target gas is tailored by the Au-loading onto MWCNTs networks. Finally, the specific metal content on functionalized MWCNT networks permits to discriminate between the three gases under test. Hence, this array based on four MWCNTs chemiresistors with controlled content of Au nanoclusters is able to identify and distinguish the three target gases. In particular, since the CNTs-based chemiresistor containing 0.3 at.% of Au shows the best response for NO₂ and NH₃, the opposite sign in the electrical response discriminates between the NH₃ and NO₂. Moreover, the metal loading allows to tune the CNTs selectivity towards a specific gaseous analyte under test.

The higher NO₂ gas sensor response of MWCNT networks containing a very low Au loading could be explained only by a chemical mechanism, because the electronic mechanism always enhances the response [59]. Therefore, since the active sites involved in the NO₂ sensing mechanism on MWCNTs are the oxygenated sites and Au NPs [49, 60]. In MWCNTs with the lowest content of Au an high content of oxygenated sites, compared to that of Au, necessary to an high NO₂ sensing

is preserved, as confirmed in Table 2 by the highest value of the ratio between the oxygen and the gold contents in XPS atomic percentages; instead, at high Au loading, the reduced relative ratio of oxygen content respect to gold content (Table 2) causes the lowering of NO₂ sensing response.

On the contrary, the H₂S sensing mechanism of Au-functionalized MWCNTs could be explained by both the electronic mechanism and the chemical mechanism. Considering the first (the electronic mechanism), it has already demonstrated that a high gold content enhances the gas sensor response; moreover, also the chemical mechanism is involved due to the great affinity between gold and sulfur atoms of thiol group [61]. In the case of the proposed H₂S sensing mechanism of Au functionalized MWCNTs, the presence of oxygenated sites is not dominant; thus the increase in the Au-NPs density enhances the amount of the adsorption sites for H₂S, resulting in a higher sensitivity and selectivity towards H₂S gas.

The gas sensing properties of pristine and Au-modified MWCNTs towards other pollutant gases, such as CO (1000-25 ppm), SO₂ (10-0.5 ppm), NO (1000-30 ppm) has also been evaluated, but, since their electrical resistance variation was very low, one order of magnitude lower (< 0.02 kΩ) than those of NO₂, NH₃ and H₂S, the responses for these gases appeared negligible and, so they were not plotted. In general, pristine CNTs are insensitive to CO gas but they can be made sensitive to CO gas by functionalizing them with carboxyl group (-COOH), as the hydrogen of anchored group will bond with the oxygen of CO molecule, thus helps in binding CO on CNT surface [62]. Moreover, H₂S gas molecules show higher response compared to SO₂ because H₂S molecules have high reducing capability than SO₂ [63]. In general, pristine MWCNTs have low sensitivity to H₂S and SO₂ gas molecules, although the presence of carboxyl groups should improve the sensitivity. On the contrary, in our case the presence of Au NPs improves only that towards H₂S since the strong interaction of Au with sulfur atoms of thiol group.

The gas sensor selectivity has been evaluated by binary gas mixtures consisting of two gases, an oxidant and a reducing one, specifically NO₂ and NH₃, and NO₂ and H₂S, in different concentration ratio, at the sensor operating temperature of 150°C, as reported in Figure 11 A and B, respectively.

The semiconducting p-type electrical transport in MWCNTs occurs depending on the opposite trend in the sensor response to the electron-donating interfering gases (NH_3 , H_2S) and the electron-withdrawing target NO_2 gas, causing a compensation of the charge transport, upon given working conditions. The compensated exchange of electrical charge affects the limit of detection (LOD) of the target NO_2 gas monitored in different real-world binary gas mixtures of reducing NH_3 and H_2S interferers. In addition, the functionalization of the MWCNT films with Au NPs enhances the sensitivity of the chemiresistor and tunes the compensation of electrical charge crossover in the selected binary ox-red mixtures. This is attributed to the combined superposition of two simultaneous competitive effects: the transfer of electrons from the reducing gas to MWCNTs film decreases the hole major carriers density, thus increases the electrical resistance, shifting the Fermi level away from the valence band; instead, in presence of an oxidizing gas, the electrons are transferred to the oxidizing gas (NO_2) from the valence band of the CNTs film with the results of the increase of hole density and, thereby, the decrease of the electrical resistance, shifting the Fermi level towards the valence band. These opposite flows in the charge transfer due to the binary gas mixture constituted by an interfering reducing gas at a fixed level and a targeted oxidizing gas at modulated concentration determine a charge compensation, at a given ratio of gases concentration.

In presence of a gas mixture composed of NO_2 and NH_3 (see Figure 11 A), for all evaluated concentration ratios, the resistance variations of all gas sensors based on pristine and Au-functionalized MWCNTs are negative: this means that all sensors are more sensitive to NO_2 compared to NH_3 , as expected due to low-sensitivity to NH_3 , as reported in Figure 10. Moreover, the highest negative resistance variations have been obtained for MWCNTs modified with Au NPs: in particular, MWCNTs networks containing the lowest Au content show the highest variations, confirming that a low Au content on CNT networks enhances the sensitivity and selectivity to NO_2 .

In presence of a binary gas mixture consisting of NO_2 and H_2S , in which the concentration ratio between NO_2 and H_2S is 5, the resistance variations for all the gas sensors are negative (see Figure 11 B): this means that all sensors are sensitive to NO_2 compared to H_2S . In the contrast, reducing

the ratio until to 1, in the case of MWCNTs with low gold content (0.3 at.%), the resistance variation is reduced but still remains negative; in the case of MWCNTs with higher gold content (0.5 at.% and 1.1 at.%), the sign in the sensor response is reversed becoming positive: this means that the dominant character of the gaseous component in the mixture depends on concentration ratio for a given functional Au content. Finally, when the concentration ratio of the two tested gases is inverted, all gas sensors are sensitive to H₂S. This trend in the dominant character of a single gas in a binary mixture was previously reported by Penza *et al.* [64] with the main features depending on both concentration ratio of a reducing/oxidizing binary mixture and Au loading on the MWCNT networked films.

These results demonstrate how reducing interfering gases affect the LOD of a targeted oxidizing gas in a real-world binary mixture, especially for very low ppb-level detection of environmental air pollutants. The compensation of the electrical charge in a real-world binary red-ox mixture at fixed level of concentration of interfering reducing gas depends on the reducing properties of the interferer, its concentration in the mixture and concentration ratio of both gases, for given sensor operating conditions. In fact, the change in the type of reducing interferer and its fixed gas concentration in the mixture modulate the sensor response according to the dominant character of the binary mixture affecting the LOD of the oxidizing gas to be sensed.

4. Conclusions

In conclusion, MWCNT-based gas sensor devices have been successfully decorated by the electrophoretic deposition of electrochemical pre-synthesized Au NPs with controlled size and loading. The novelty of the proposed method consists in a fine control of the quantity of deposited Au NPs by tuning the time of the electrophoresis, avoiding the clustering of Au NPs. The surface modification of the MWCNT networks with Au NPs has improved the NO₂ gas sensitivity up to the detection of sub-ppm levels. The effects of tailored Au loading onto the CNT surface on gas sensitivity and selectivity have been evaluated, revealing the highest NO₂ sensitivity for CNTs

containing the lowest Au content, and excellent H₂S sensitivity for CNTs with the highest Au loading, depending on the different proposed sensing mechanisms (chemical and electronic) of the two analyzed gases. Therefore, for the first time it has demonstrated the total surface amount of deposited Au NPs controls the MWCNT sensing capabilities. Specifically, the sensing properties are controlled by the superficial chemical composition since a decrease in the ratio between the XPS oxygen content respect that of gold causes a decrease of NO₂ sensitivity and, on the contrary, an increase of that towards H₂S gas.

Finally, the selectivity of MWCNT-based gas sensors has been evaluated by binary mixtures consisting of the oxidizing target NO₂ gas and a reducing interfering gas (NH₃ and H₂S). Therefore, the fine tune of the metal loading on MWCNTs has allowed to control not only the gas sensitivity but also the selectivity towards a specific gaseous analyte.

Summarizing, this work wants to demonstrate that the functionalization of MWCNT-based gas sensor by Au NPs is not at all sufficient to improve its sensitivity and selectivity towards a definite gaseous analyte, but a fine tuning of the surface concentration of deposited Au NPs permits to control the gas sensor properties.

The proposed electrochemical functionalization process of MWCNTs is fast and seems to be easily applicable for low-cost mass-production of modified MWCNT-based gas sensors.

This is actually a proof-of-concept study, providing for the first time evidences of the possible use of electrophoretic procedures to bring preformed nanocatalysts on the surface of CNTs for gas sensing applications. Investigation of the humidity factor will be subject of further study. Moreover, future work on different metal surface-modifications of the carbon nanotube networked films is planned for specific gas detection in sensor arrays concerning environmental monitoring applications at sub-ppm level in the real world.

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Figure caption

Figure 1. TEM images of A) electrochemically synthesized core-shell Au NPs; B) MWCNTs networks grown by RF-PECVD with Co-catalyst onto alumina substrate (the raw nanomaterial is mechanically removed from substrate for TEM observations).

Figure 2. Schematic view of the two-pole chemiresistor based on MWCNTs networks surface-functionalized with Au NPs.

Figure 3. A) XPS core level spectra of C1s in pristine (i) and functionalized MWCNTs (ii) and peaks resulting from a fitting procedure, using green for sp^2 carbon, red for sp^3 amorphous carbon, dark blue for C-O and orange for π -plasmon excitations. B) XPS core level spectrum of Au 4f in functionalized CNTs.

Figure 4. SEM images of A) pristine MWCNTs, and MWCNTs decorated with B) 0.3 at.%, C) 0.5 at.%, and D) 1.1 at% Au loading.

Figure 5. TEM images of MWCNTs decorated with Au NPs. Scale bar is 50 nm on the left image, 20 nm for all the other images.

Figure 6. Responses of four chemiresistors based on (a) pristine MWCNTs, and on functionalized MWCNTs with (b) 0.3 at.% Au loading, (c) 0.5 at.% Au loading, and (d) 1.1 at.% Au loading, exposed to repeated 10 min pulses of individual gas concentrations, specifically, of 10 ppm and 0.1 ppm of NO₂, 1000 ppm and 5 ppm of NH₃, 10 ppm and 0.1 ppm of H₂S, at sensor temperature of 150°C.

Figure 7. Mean sensitivity of pristine and Au-decorated MWCNTs-based sensors toward NO₂ gas at different sensor operating temperatures in the range 100–200°C.

Figure 8. Time response of chemiresistors based on pristine MWCNT films, and functionalized CNTs films with Au loading of 0.3 at.%, 0.5 at.% and 1.1 at.%, exposed to 10 min pulses of decreasing concentrations of (a) NO₂, (b) NH₃ and (c) H₂S at a sensor temperature of 150°C.

Figure 9. Calibration curves for chemiresistors based on pristine MWCNTs networks, and functionalized CNTs networks with Au loading of 0.3 at.%, 0.5 at.% and 1.1 at.% exposed to (a) NO₂, (b) NH₃, and (c) H₂S, at a sensor temperature of 150°C.

Figure 10. Comparison of mean sensitivity for four chemiresistors based on pristine and functionalized MWCTs with Au loading of 0.3 at.%, 0.5 at.% and 1.1 at.%, exposed to NO₂, NH₃ and H₂S gases, at a sensor temperature of 150°C. The concentration range for NO₂, NH₃ and H₂S gases is 0.1–10 ppm, 5–1000 ppm, and 0.1–10 ppm, respectively.

Figure 11. Time response of chemiresistors based on pristine and functionalized MWCNTs with Au loading of 0.3 at.%, 0.5 at.% and 1.1 at.%, exposed to 10 min pulses of variable NO₂ concentrations (5–0.1 ppm) mixed with **A**) NH₃ at a fixed concentration of 25 ppm, and **B**) H₂S at a fixed concentration of 1 ppm, at a sensor temperature of 150°C.

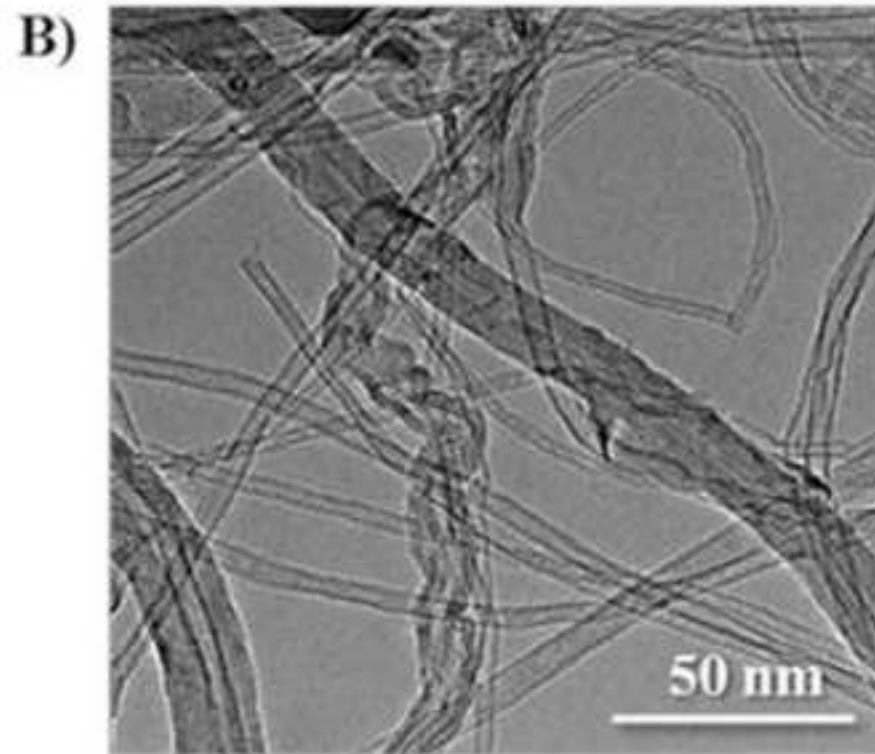
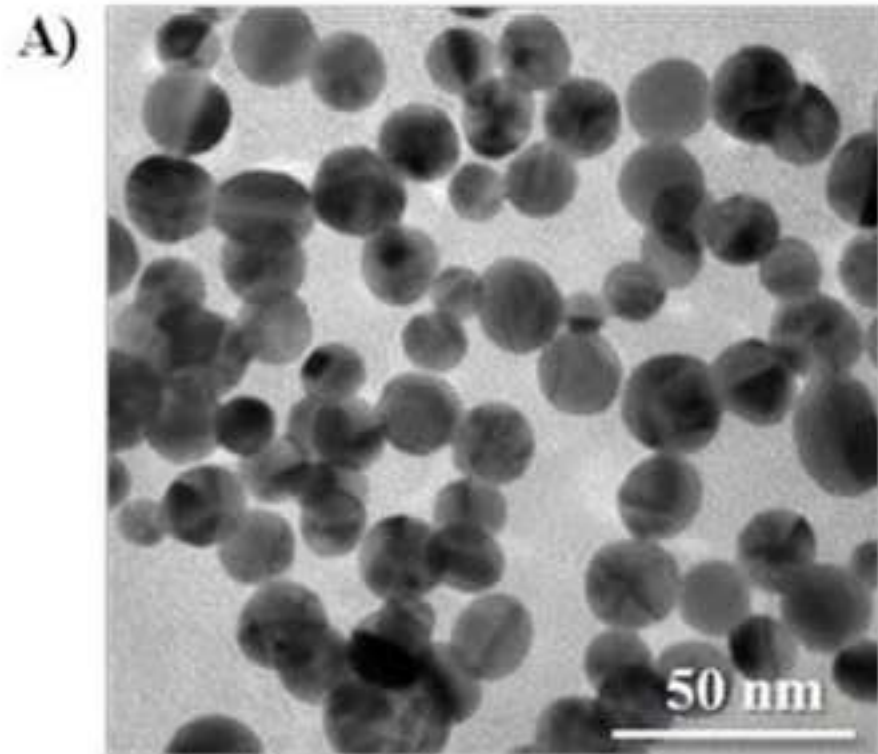
Table 1. Relevant gas sensing responses reported in literature regarding the use of Au-decorated MWCNTs as gas sensor

Au deposition method	Gaseous analyte @ lowest tested concentration	Operating Temperature (°C)	Response (%)	Sensor system	Ref.
Electron-beam evaporation	NH ₃ @ 4 ppm	Room temperature (Recovery under UV light illumination or annealing)	0.125	Chemiresistor	[32]
Electrochemical deposition	H ₂ S @ 2 ppb	Room temperature	3.75	FET	[33]
Sputtering deposition	NO ₂ @ 0.5 ppm	200°C	2.0	Chemiresistor	[34]
	NH ₃ @ 5 ppm		0.1		
Thermal evaporation	H ₂ S @ 0.1 ppm	150°C	4.5	Chemiresistor	[35]
	NO ₂ @ 1.5 ppm		7.4		
	NO ₂ @ 0.5 ppm		4.2		
Physical deposition	C O @ 5ppm	Room Temperature (Recovery @ 80°C)	2.5	ID Chemiresistor	[37]
	NO ₂ @ 0.5 ppm	30°C (Recovery @ 150°C)	2.0	Chemiresistor	[38]

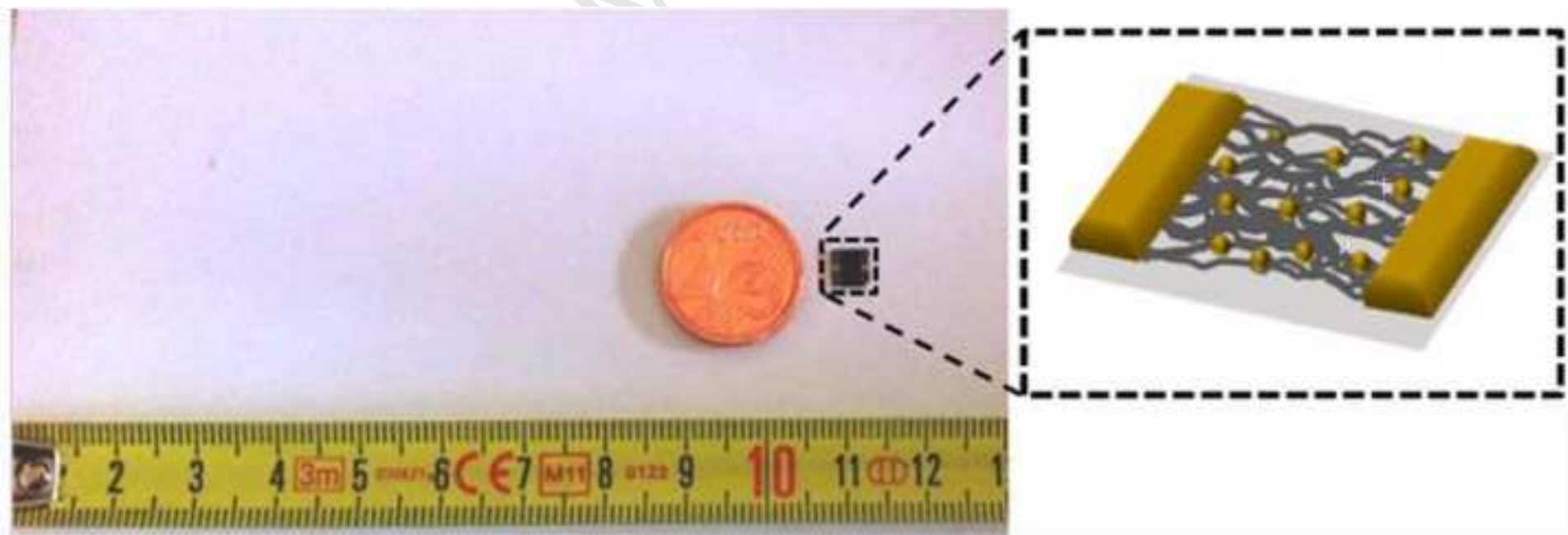
Table 2. XPS surface chemical composition of pristine and Au-functionalized MWCNTs.

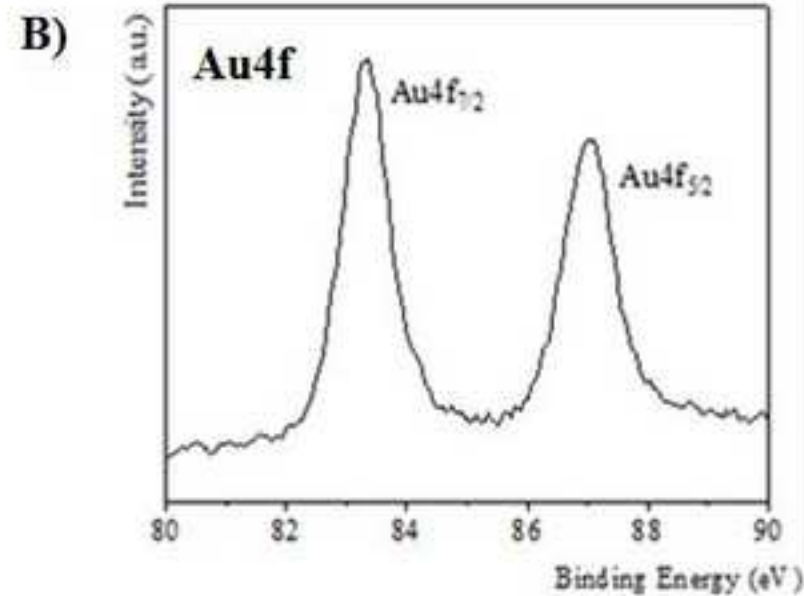
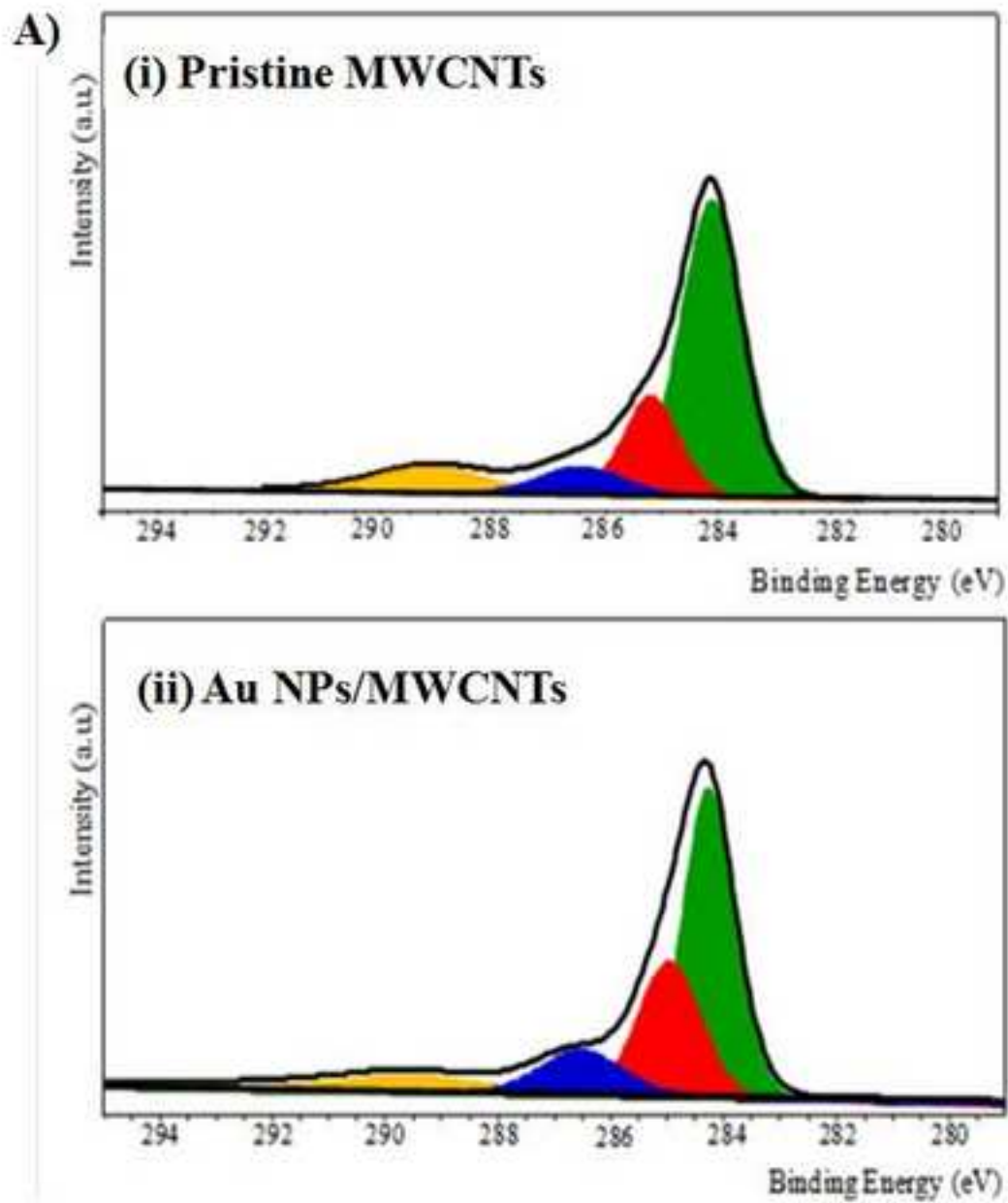
SAMPLE	C (at.%)	Au (at.%)	O (at.%)	O (at.%) / Au (at.%)
Pristine MWCNTs	95.0 ± 0.5	-	5.0 ± 0.5	-
Au NPs/MWCNTs t: 90 s	94.4 ± 0.5	0.3 ± 0.2	5.3 ± 0.5	18
Au NPs/MWCNTs t: 300 s	92.0 ± 0.5	0.5 ± 0.2	7.5 ± 0.5	15
Au NPs/MWCNTs t: 600 s	91.2 ± 0.5	1.1 ± 0.2	7.8 ± 0.5	7

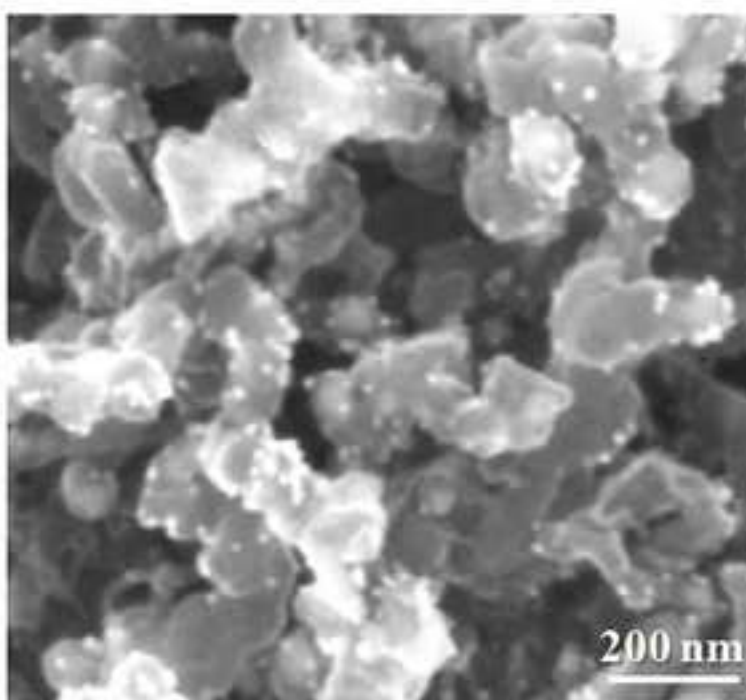
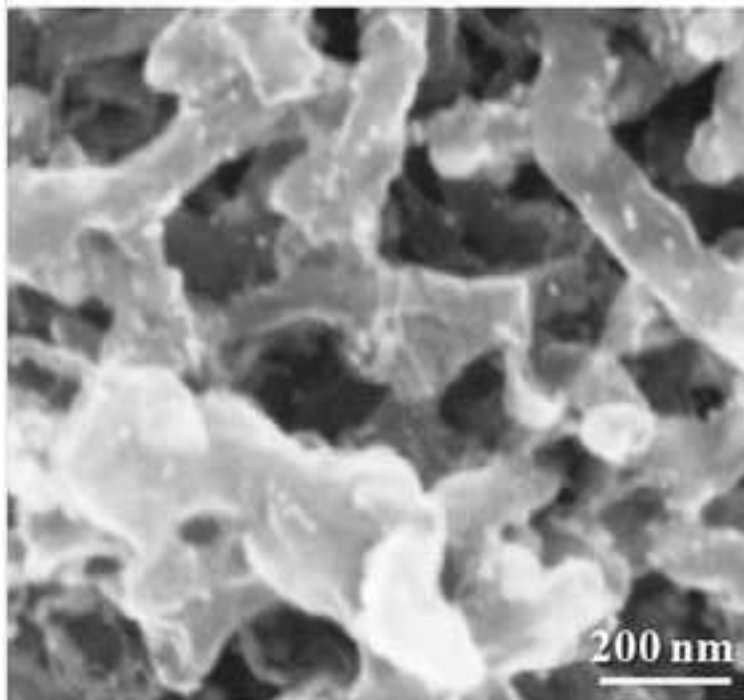
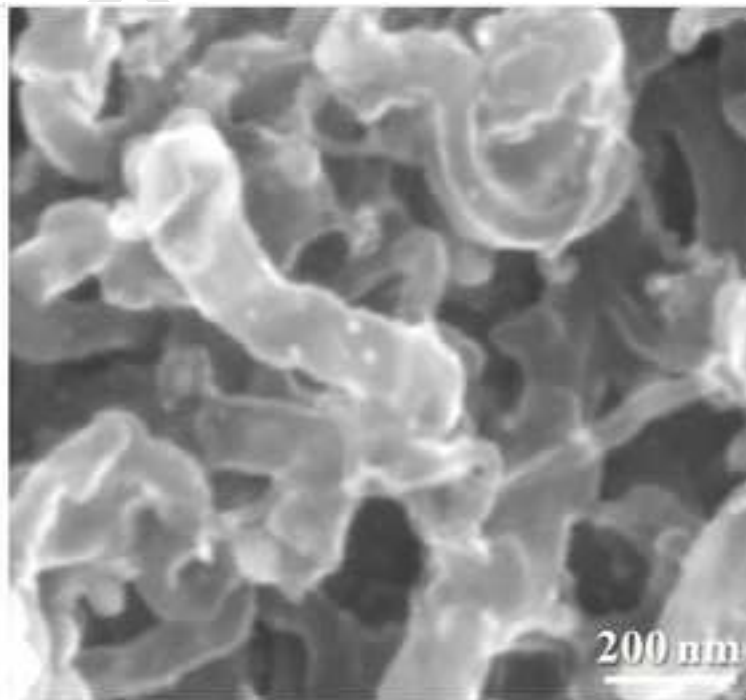
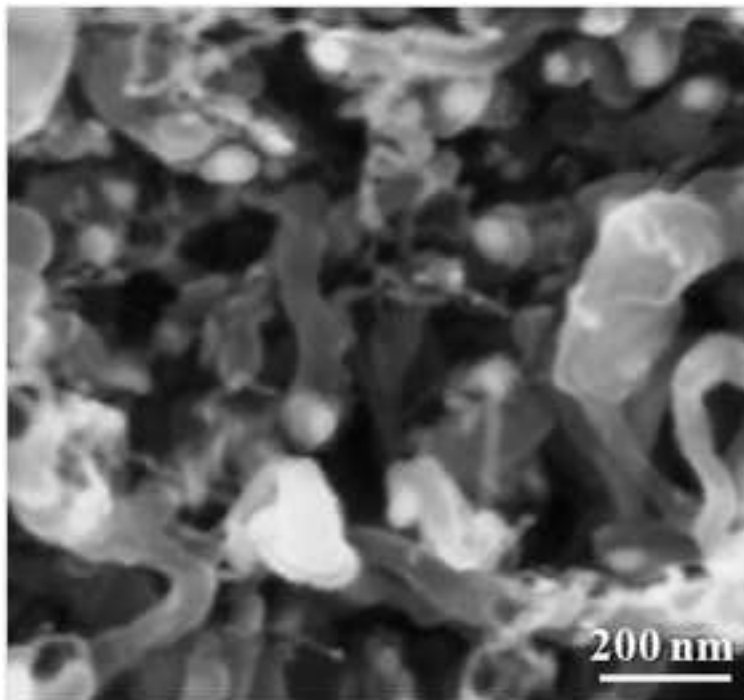
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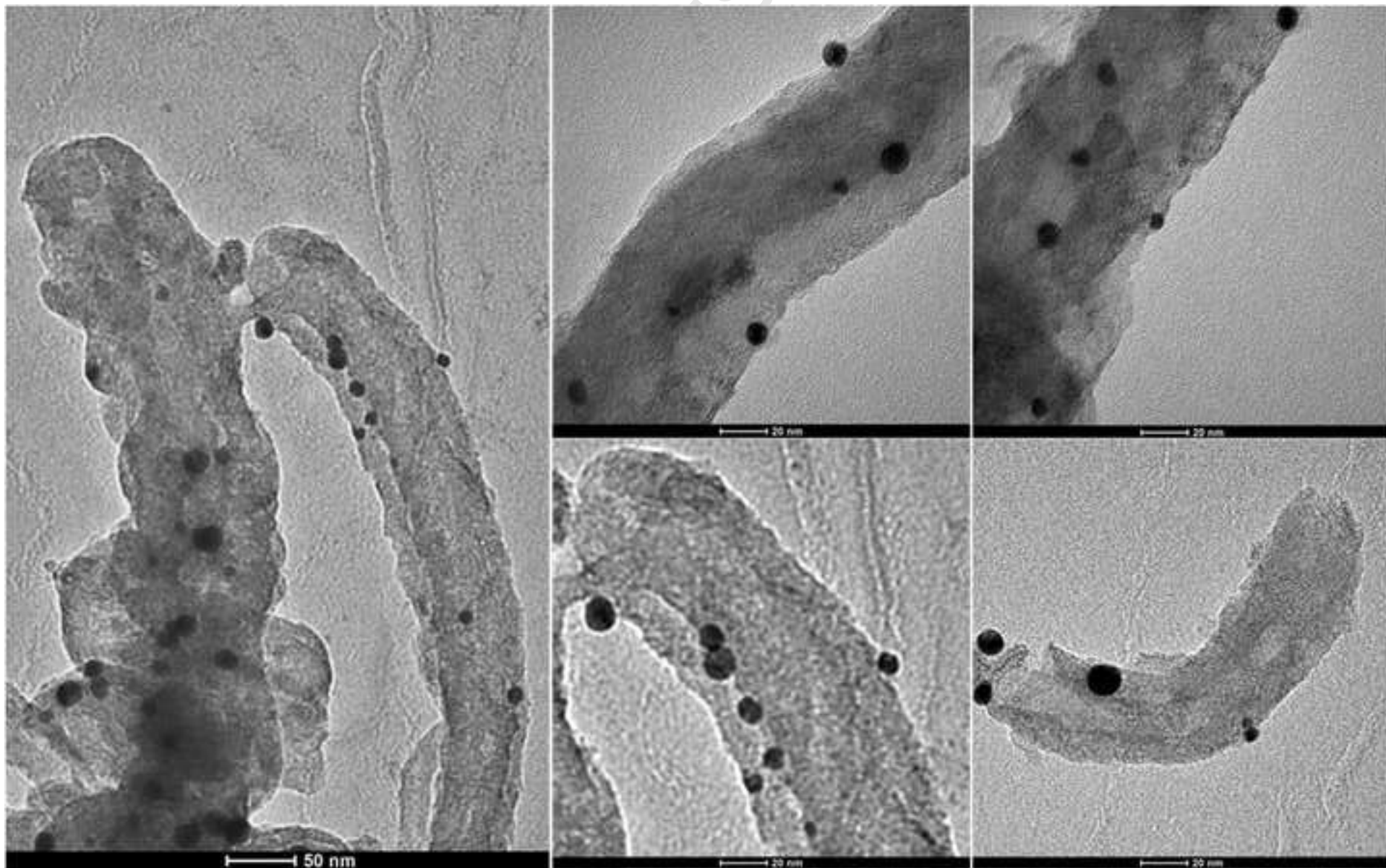


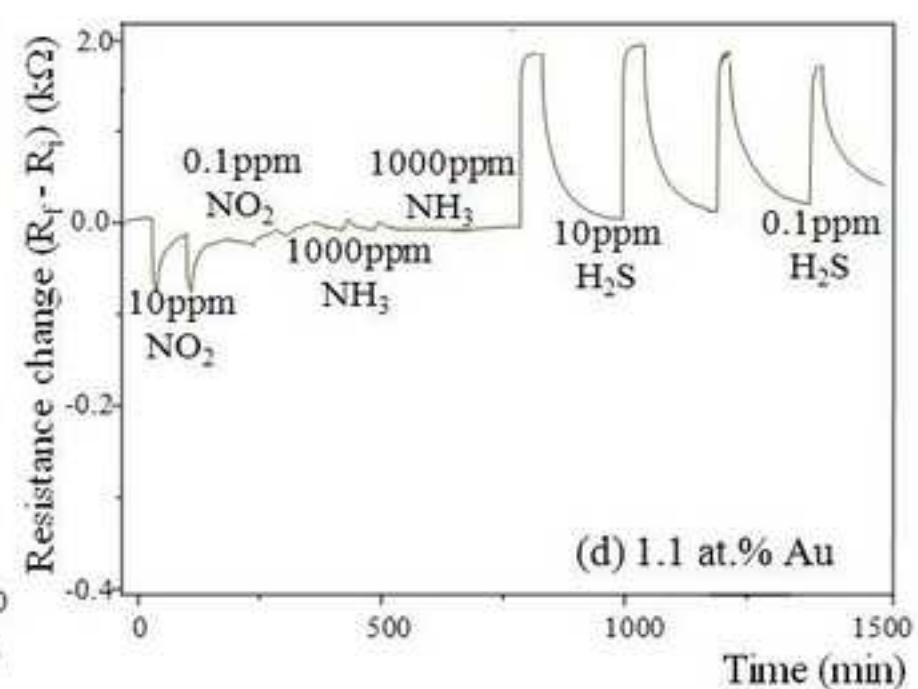
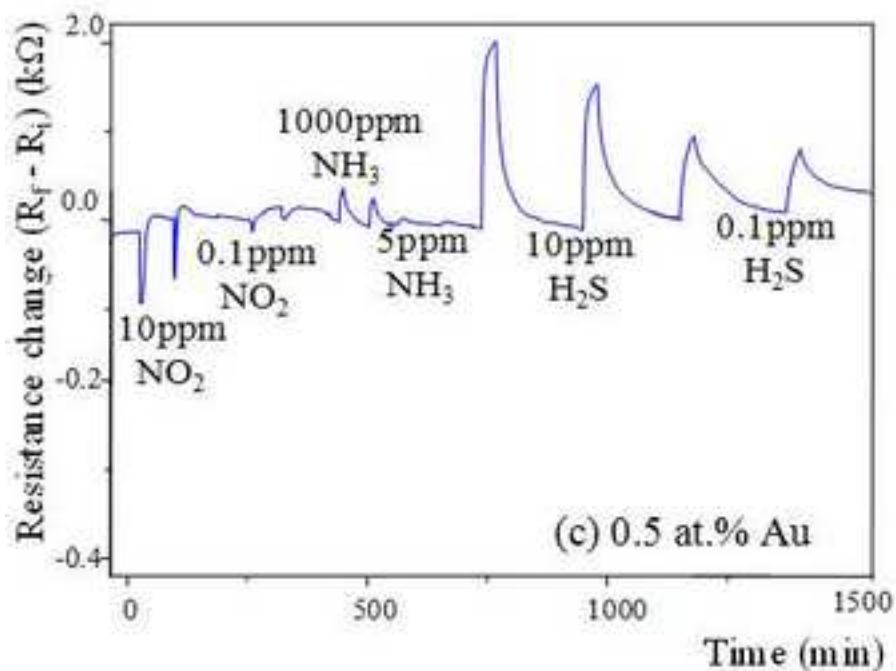
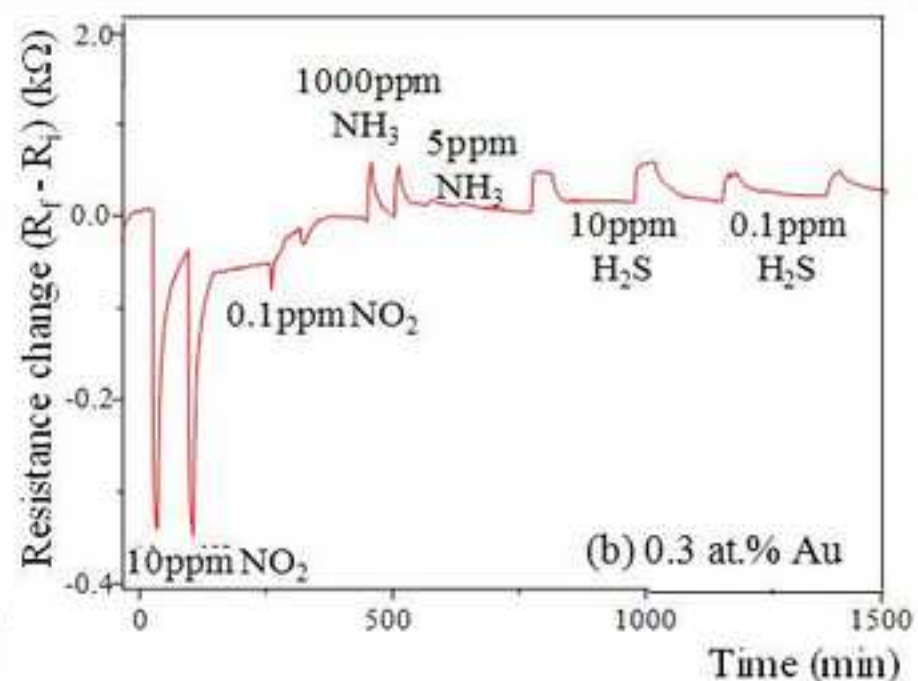
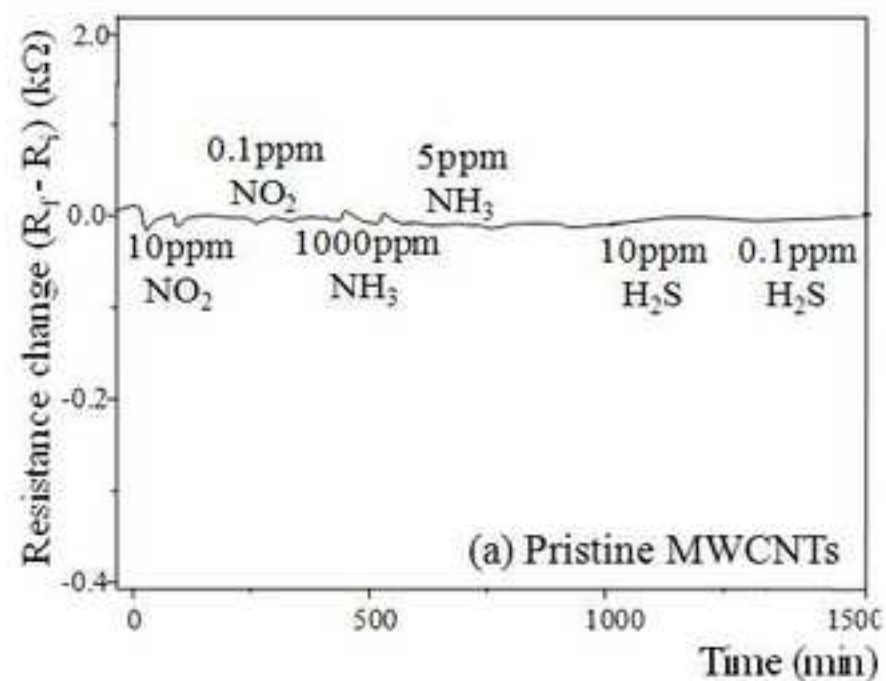
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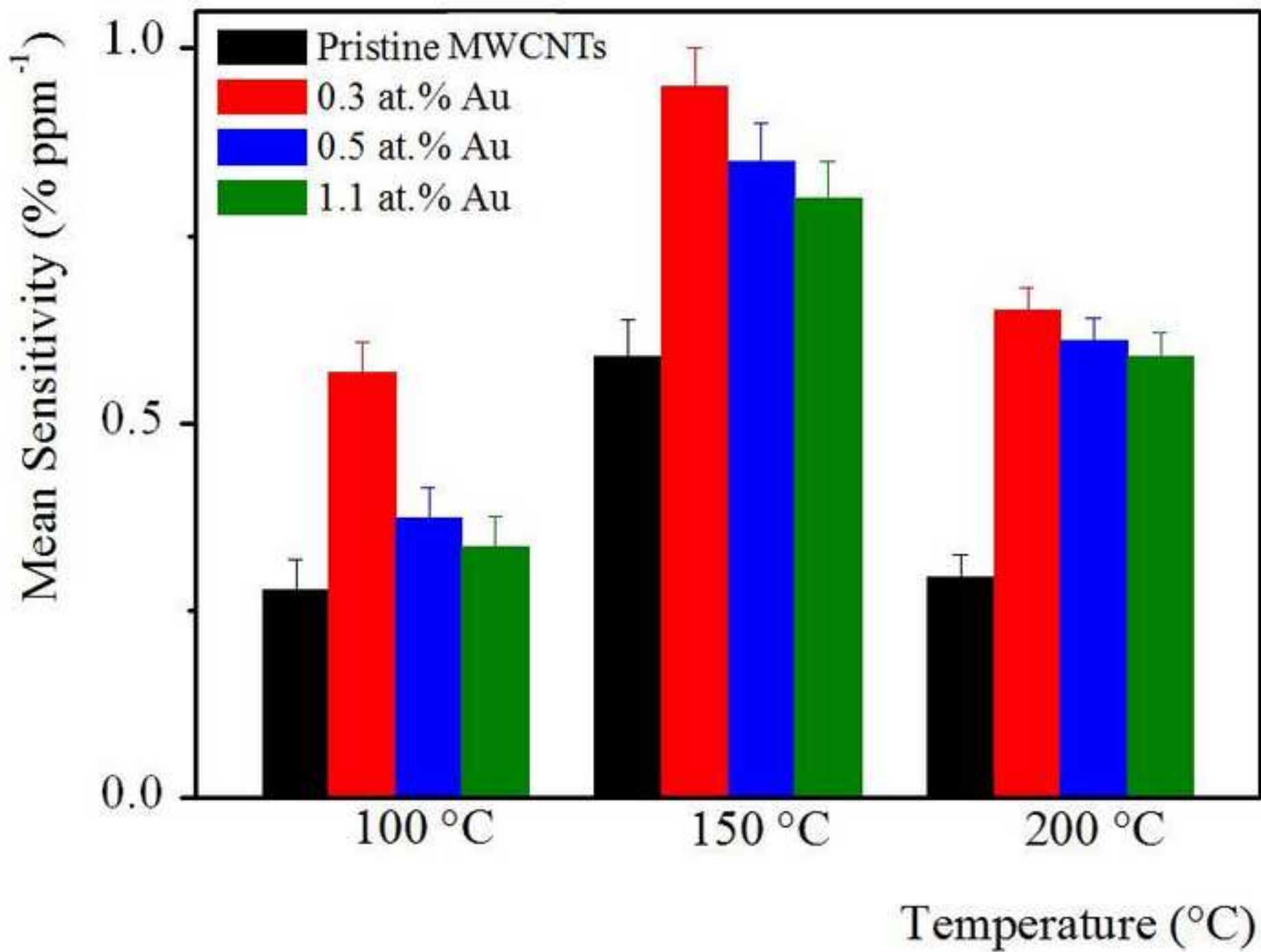


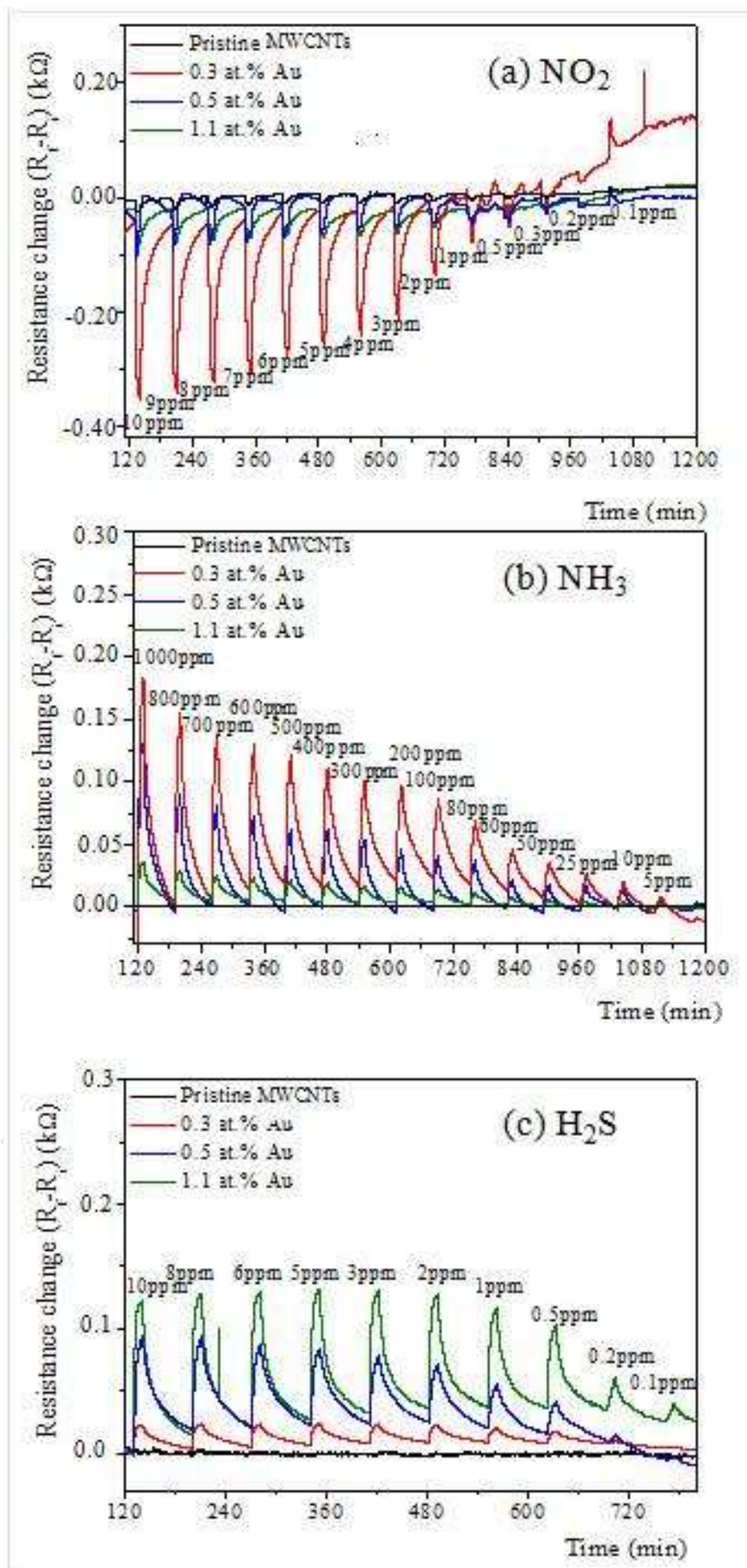


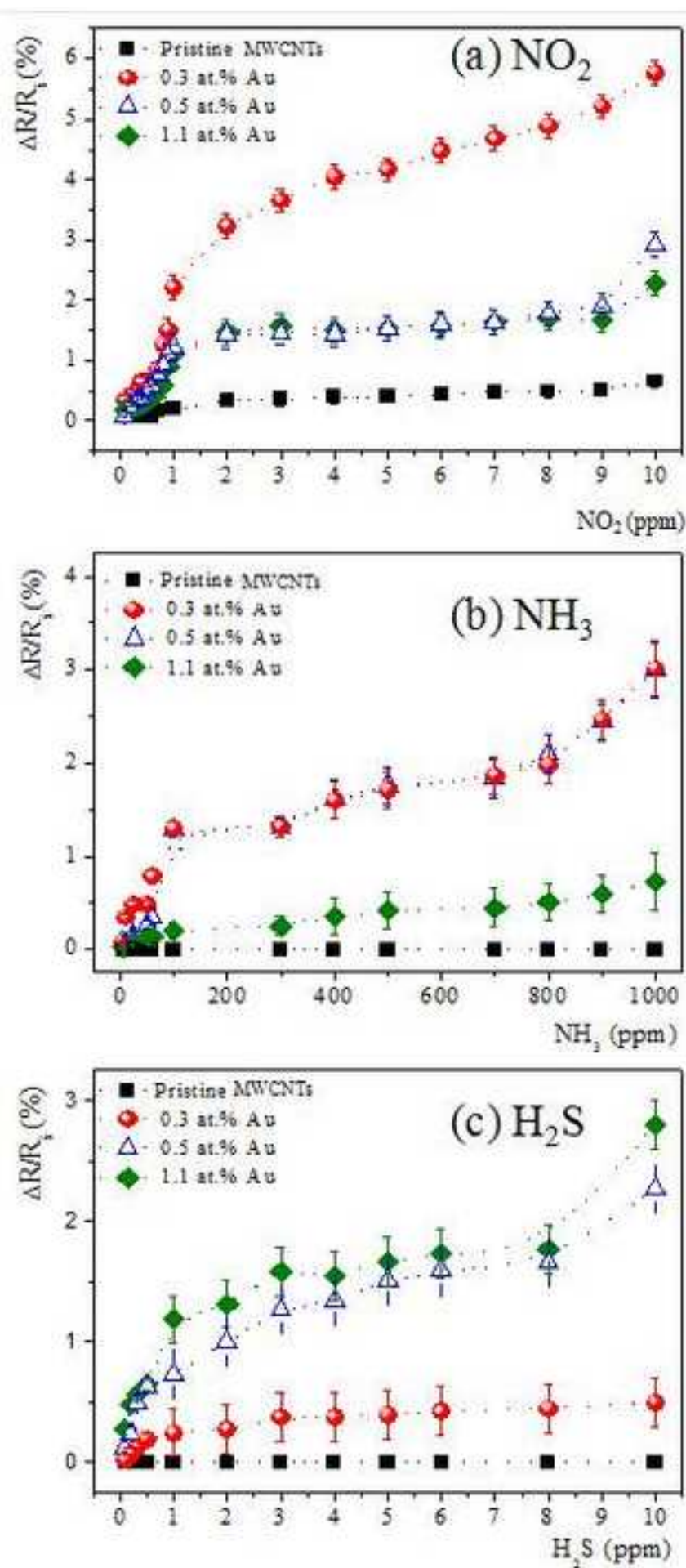


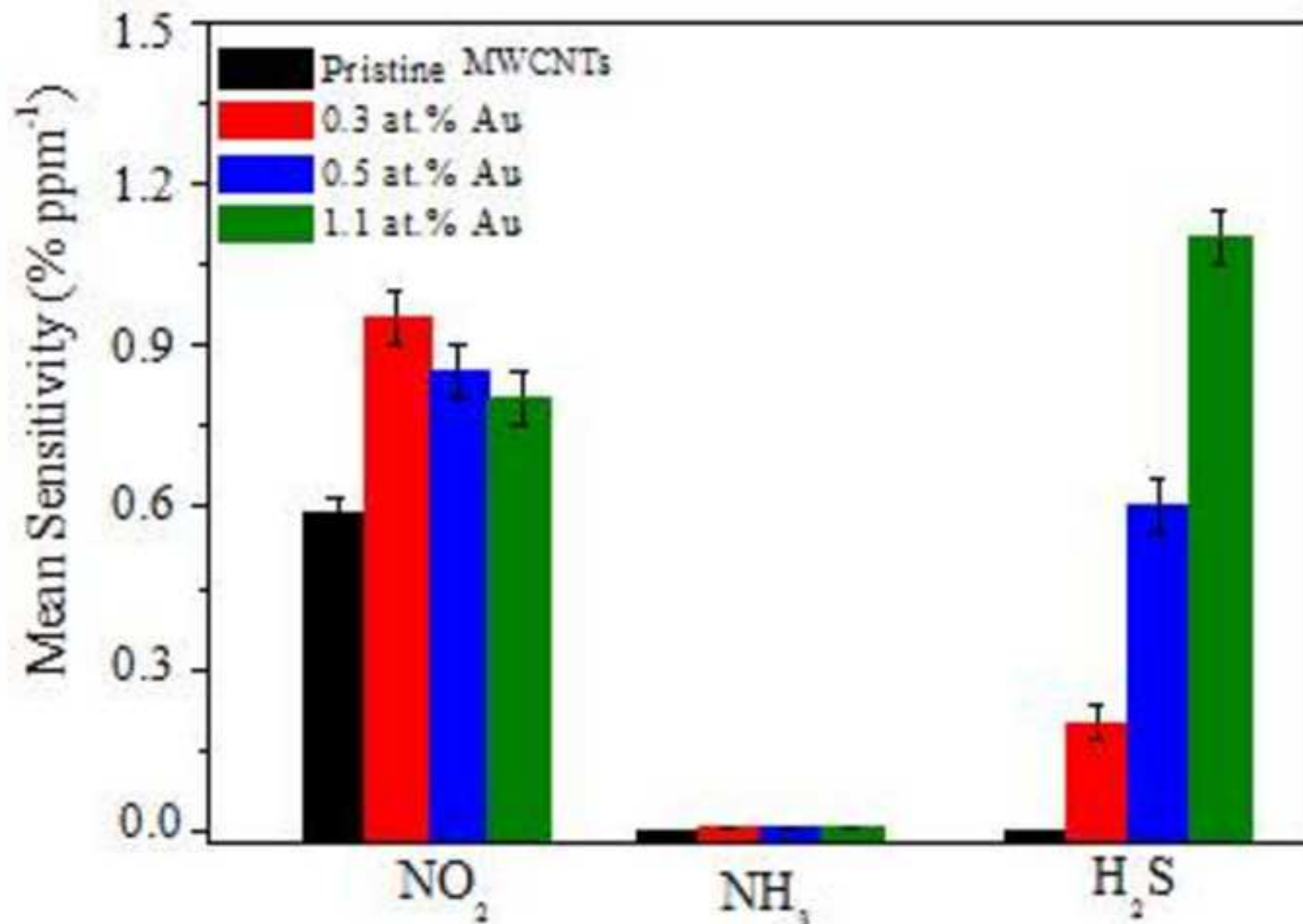


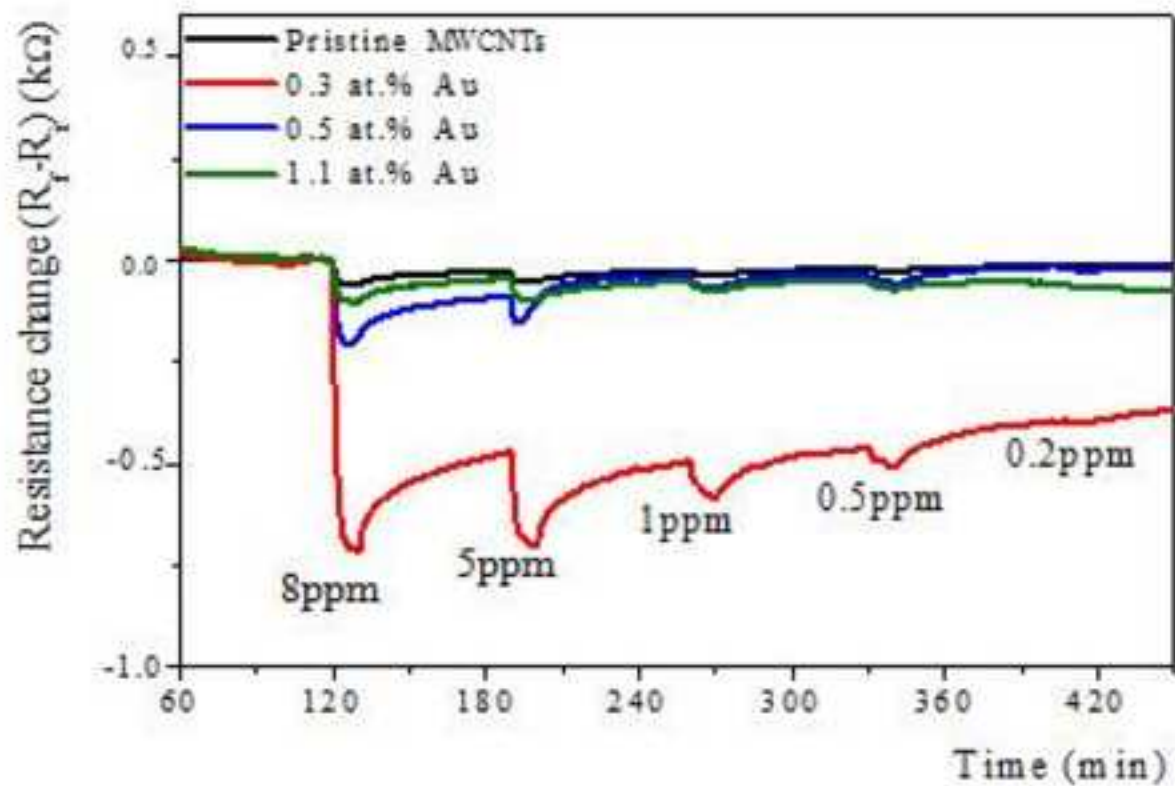
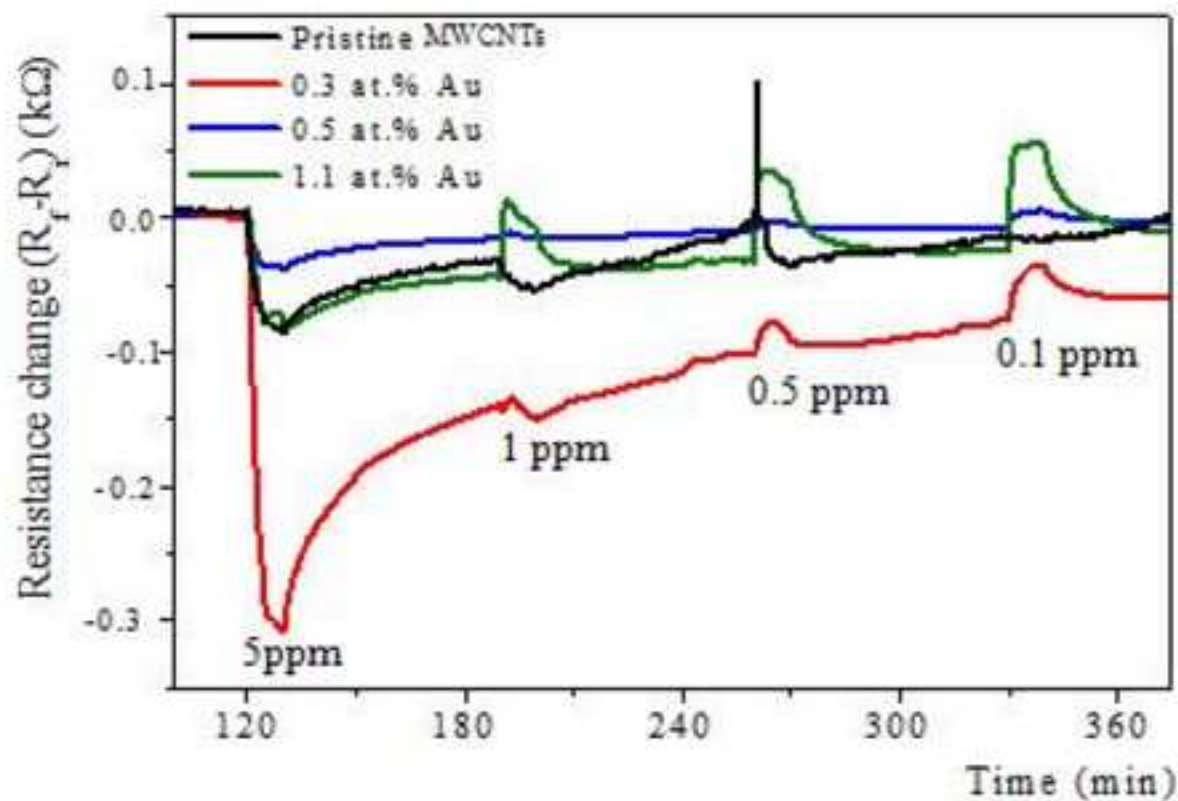










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Prof. Nicola Cioffi is Assistant Professor at the University of Bari. He serves as referee for 25 international journals and is member of the Editorial Board of the journals *Research & Reviews in Electro Chemistry*, *Sensor Letters*, and *The Open Materials Science Journal*. His research interests are in the field of nanomaterials for the life science, including gas- and bio-sensors, antibacterial/bioactive nanomaterials, catalysts for green chemistry, and surface analysis of novel materials. He serves as referee for 27 international journal and is a member of five Editorial Boards. He co-edited special issues of *Sensor Letters* and *Molecules* journals. His scientific output includes several invited seminars, book chapters, papers and editorials in peer-reviewed journals and textbooks, 2 European patents, and 150 conference communications.