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Abstract
The response to relative humidity (RH) and alcohol vapors of resistive-type sensors based on nanobeads of conjugated polymers, namely polyphenylacetylene (PPA) and copolymer poly[phenylacetylene-(co-2-hydroxyethyl methacrylate)] (P(PA/HEMA)), were investigated. Sensors based on ordered arrays of these nanostructured polymeric materials showed stable and reproducible current intensity variations in the range 10–90% of relative humidity at room temperature. Both polymers also showed sensitivity to aliphatic chain primary alcohols, and a fine tuning of the sensor response was obtained by varying the chain length of the alcohol in relation to the polarity. The nanostructured feature of polymeric-based membranes seems to have an effect on the sensing response and an enhancement of the sensitivity was observed for the response to water and alcohol vapor variations with respect to previous studies based on amorphous polyphenylacetylene. High stability of the polymeric nanostructured membranes was detected with no aging after two weeks in continuum stressing measurement conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Conjugated polymers, such as polyacetylene (PA) and their derivates, are polymers in which the main chains consist of alternate single and double bonds, which leads to broad π-electron conjugation. They show conductive or semiconductive properties, have been used as the active layers of gas sensors since the early 1980s [1] and, in comparison with most of the commercially available sensors, based on metal oxides usually operating at high temperatures [2, 3], the sensors made from conjugated polymers have many improved characteristics. In fact, the polymers show high sensitivity and short response times at room temperature compared to the response of commercial sensors, and can be obtained by easy synthesis procedures and facile modification of the molecular chain structure by copolymerization or structural derivations. Furthermore, conjugated polymers have good

mechanical properties, which allow simple fabrication of sensors [4, 5]. Several reviews emphasize different aspects of gas sensors [6, 7] and the new strategies are focusing on the fabrication of devices that are fast, nondestructive and low cost. The literature reports several types of sensors, and among them some attractive ones are resistive sensors, based on the change of the electrical resistance of semiconductive films when exposed to VOC (volatile organic compounds) vapors [8]. In any case the sensing phenomenon is a surface effect of gas–solid interaction [9] and a large specific surface area of the sensing material is essential for obtaining high sensitivity. Nanospherical particles with diameters about 100–200 nm, exhibiting a large surface area, might be favorable for improving the performance of gas sensing materials [10]. Besides, in order to improve the selectivity for a particular application, surface modification by a proper choice of additive to the pristine materials or preparation of copolymers is used [11–13]. In some initial studies, it has been observed that PPA and P(PA/HEMA) nanospheres, synthesized by the

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emulsion polymerization technique [14], possess excellent gas sensing responses to water [15] with respect to amorphous PPA [16].

In this work, an investigation of the vapor sensing properties of phenylacetylene (PPA) nanospheres, whose chemical structure is shown in figure 1(a), was carried out. In order to improve the superficial charge of the materials, 2-hydroxyethyl methacrylate (HEMA) was copolymerized with phenylacetylene (PA), leading to P(PA/HEMA) nanostructured copolymer (chemical structure is reported in figure 1(b)) that was tested as an active membrane towards water, methanol, ethanol, n-propanol and n-butanol vapors.

2. Experimental details

2.1. Materials and instruments

The nanobeads of PPA and P(PA/HEMA) were obtained by the modified emulsion synthesis technique as reported in our previous work [14]. Besides routine physical–chemical characterizations, particle morphology, dimensions and self-assembling were closely investigated on metalized samples by SEM (scanning electron microscopy) using an SEM-LEO1450VP instrument. The images were recorded using an image analysis software tool (Scion Image for Windows, Scion Corp, Beta 4.0.2) (see figures 1(a) and (b)). The devices used to perform the electrical characterizations of the polymeric nanobeads were prepared using silicon ⟨100⟩ passivated with SiO_2 (thermally grown) substrates where 40 pairs of interdigitated chromium electrodes had been evaporated and photolithographically defined (thickness 200 nm, interdigitated finger distance and width 20 μm). Water suspensions of polymers PPA and P(PA/HEMA) (10 mg ml^{-1}) were cast-deposited onto the silica substrates at room temperature. The electrical responses of the devices were analyzed by dc measurements at 23 ± 0.5 °C in a chamber (volume 15 cm^3) made of a water repellent and chemically resistant material. Relative humidity was measured by using a commercial sensor (Honeywell HIH 3602 C), which gave an accuracy of $\pm 1\%$ in the range considered for our measurements. The current response due to RH variations (from 10 to 90%) for a fixed value of applied voltage at the electrodes was recorded. Before each set of measurements the sensor was exposed to dry N_2 flow for 1 h in order to check the initial dc electrical resistance and to find the baseline of the sensing devices. All measurements were performed in dark conditions. Relative humidity was changed in steps of 2.5% every 300 s ($T s$). The current intensity variations were measured using a Keithley 595 Quasistatic CV Meter Instrument, with a fixed applied voltage of $+1$ V. In order to calculate the value of the saturated expression (P_S) and to get the ppmv values for each alcohol considered (methanol, ethanol, n-propanol and n-butanol), we have utilized the Antoine equations:

$$\text{Log}_{10}(P_S) = A - (B/(T + C)) \qquad \text{ppmv} = P_S/(P_T - P_S)$$

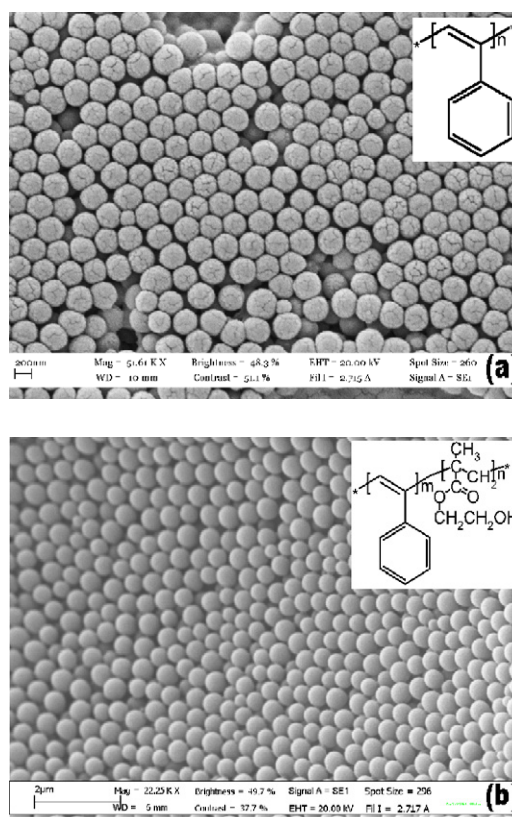where A, B and C are parameters reported in the literature [17].

Figure 1. SEM image of PPA (a) and of P(PA/HEMA) (b) nanobeads.

Two MKS mass flow controllers, that can operate in the range 0–200 sccm (standard cubic centimeters per minute) were used for gas flux regulation. A total gas flow of 200 sccm passed through the measurement chamber by imposing this relationship between fluxes: wet-flux + dry-flux = 200 sccm. According to the manufacturer's specification, the accuracy of the flow meter is better than 1% at maximum flow. A temperature and humidity sensor (Honeywell HIH 3602 C) was used to monitor RH and to measure temperature stability in the testing cell. Dynamic variations of the alcohol fluxes were obtained with the MKS mass flow controllers by introducing into the cell a stream of nitrogen mixed with the alcohol vapor in the proper ratios. Chemical testing cycles consisted of target gas exposures for a given time to reach a steady state of the sensor signal, alternating with a purge run of proper duration in order to re-establish the baseline signal and recover the sensor output signal. The set-up of the experimental apparatus for resistive-type measurements is depicted in figure 2.

3. Results and discussion

3.1. Response to humidity

Preliminary investigations on humidity sensors based on nanostructured PPA and P(PA/HEMA) membranes deposited on Cr electrodes showed fast and reproducible current intensity variations in the range RH 10–90% [15]. More in-depth studies have now been performed and we have observed
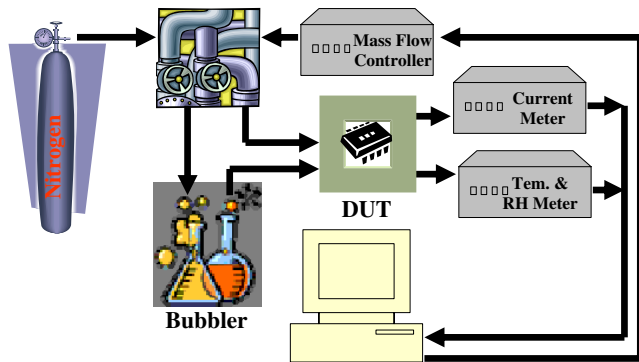
Figure 2. Scheme of the apparatus used for electrical/sensory characterizations.
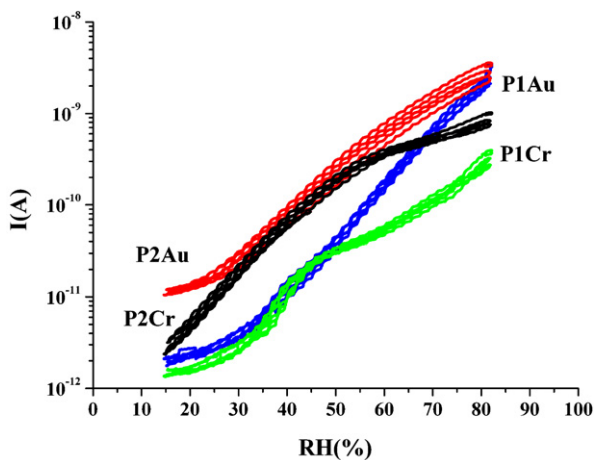

Figure 3. Current intensity versus RH (%) for nanostructured polymers PPA(P1) and P(PA/HEMA) (P2) on different interdigitated electrodes (Au, Cr) with 1 V applied voltage.

Figure 4. (a) Current intensity versus time in on/off cycles for nanostructured polymers. ON: RH = 18% 1 h. OFF: RH = 80% 1 h. (b) Single cycle. The curve represented by -■- indicates the response of the commercial sensor.

a slight improvement of the response of the sensors based on nanostructured PPA and P(PA/HEMA) deposited onto Au electrodes. In figure 3, a comparison of the responses of nanostructured PPA and P(PA/HEMA) on chromium and gold electrodes towards RH % variations is reported. The reproducibility of the measurements performed on the nanostructured PPA and P(PA/HEMA) sensors is noteworthy; current intensity values were reproduced when recorded in different cycles of measurements, in which the same RH percentages were reached in the test chamber, as reported in figure 4. In these cycles, the RH variations were obtained by maintaining RH at fixed values for a given time (usually 1 h) and by increasing the RH values from 10% to 75% in successive runs. The mechanism of interaction between substituted polyacetylenes and H_2O molecules may be interpreted on the basis of previous XPS studies performed on amorphous polyphenylacetylene membranes [16]: for these materials, which behave as a sponge for humidity, the interpretation of the electrical response is based on the diffusion processes of water in the vapor phase inside the nanostructured matrix. In fact, the nanostructure improves this behavior by increasing the superficial area for the achievement of interactions.
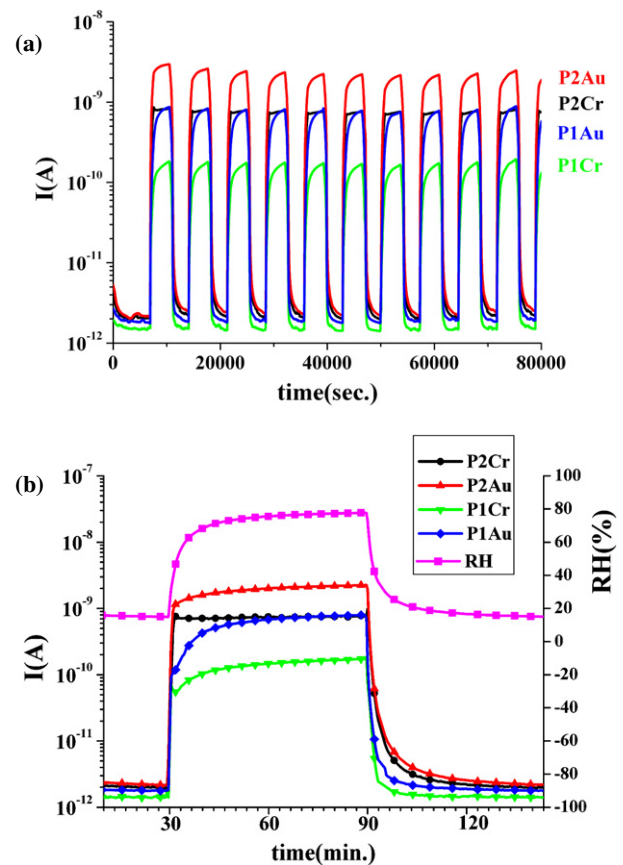
3.2. Response to alcohols

In order to extend our investigations to VOC vapors, polymeric membranes were exposed to selected primary alcohol vapors, i.e. methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH) and n-butanol (n-BuOH). When alcohol vapors were bubbled onto polymeric devices, a variation of the electrical response was observed for the two nanostructured systems, PPA and P(PA/HEMA). Before the measurements, sensors were stabilized in an atmosphere of dry nitrogen for 1 h. The polymer membranes were then exposed to a nitrogen stream charged with alcohol vapor and the corresponding electrical response was measured in subsequent cycles lasting approximately 7 h each. Both polymers showed sensitivity to aliphatic chain primary alcohols, in the range of ppmv from 0 to the maximum value allowed by the vapor tension (PS), which is a physical property of each investigated alcohol. Due to the low reactivity of many organic compounds, included the analytes examined in this work, it is generally difficult to detect VOCs by chemical reactions at room temperature. However, it is still possible to detect alcohols by their weak physical interactions with the sensing polymers, involving absorbing or swelling of the polymer matrices [18]. A tuning of the sensor response was detected depending on the alcohol chain length, which is in turn related to alcohol polarity, and this is
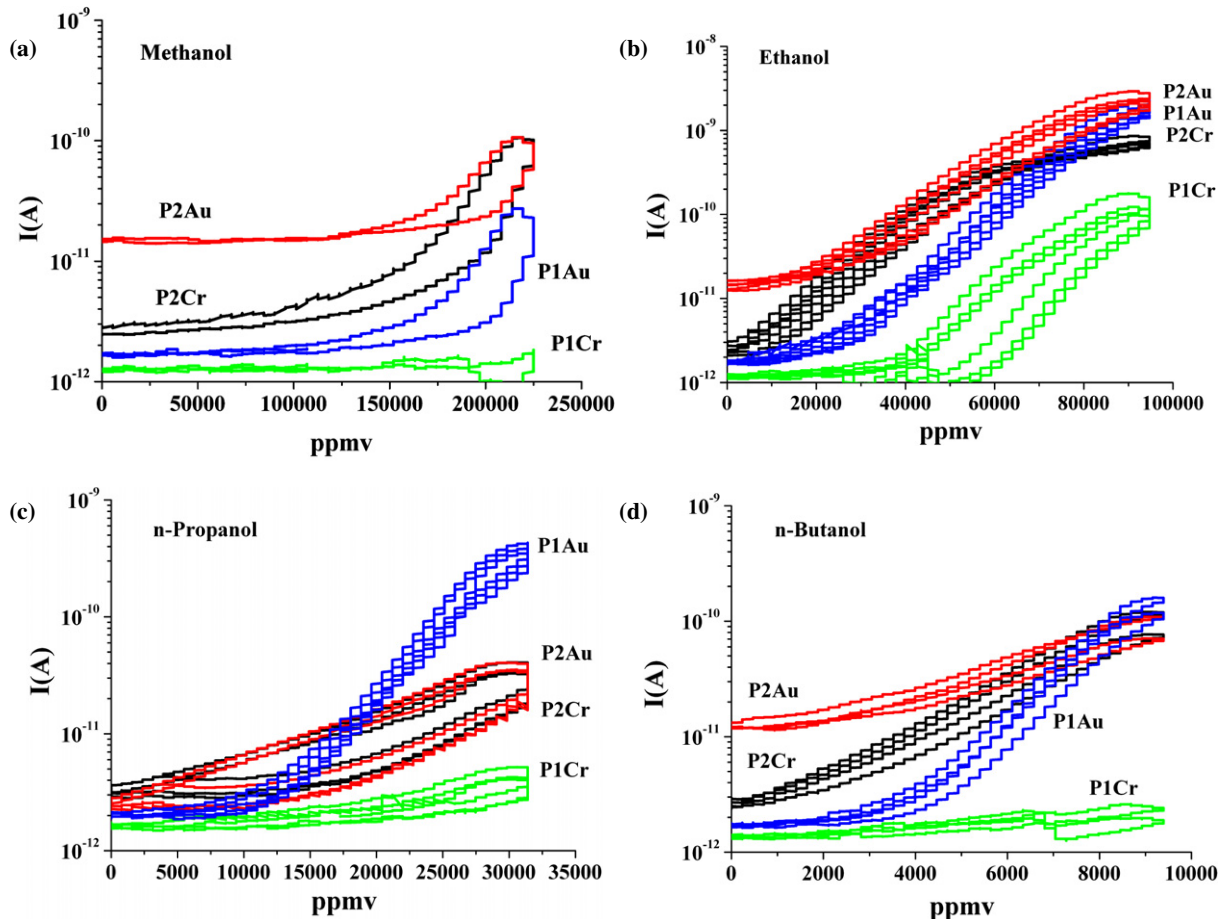
Figure 5. Current intensity versus alcohol vapor concentration for nanostructured polymers PPA(P1) and P(PA/HEMA) (P2) with different electrodes: (a) methanol CH_3OH, (b) ethanol CH_3CH_2OH, (c) n-propanol $CH_3(CH_2)_2OH$, (d) n-butanol $CH_3(CH_2)_3OH$.

probably due to the higher affinity of nanostructured polymeric membranes to materials with lower polarity; for example, in this case, butanol shows enhanced response and sensitivity in comparison with the other investigated alcohols. The sensors were tested in subsequent different cycles in an extended range of ppmv for the different alcohols, after two weeks in continuum stressing measurement conditions, and no aging or degradation of their performance was observed.

The response curve of the sensors based on nanostructured PPA and P(PA/HEMA) cast-deposited onto Au or Cr interdigitated electrodes, exposed to alcohol vapors, is shown in figures 5(a)–(d).

By comparing the results shown in figures 5(a)–(d), we can discriminate between the responses of the sensors to different alcohols. The measurements of current intensity upon exposure of the sensors to MeOH, an alcohol with a short aliphatic chain and high polarity, reveal a low sensitivity of the device regardless of the nature of the metal electrode (Au, Cr) and of the polymeric membrane, while EtOH, n-PrOH and n-BuOH, alcohols with longer aliphatic chains and lower polarity, showed a variation of 2–3 orders of magnitude of the current intensity in the considered ppmv range. Figure 6 points out these different responses of P(PA/HEMA) in the case of using Cr electrodes towards the chemicals under test, i.e. methanol, ethanol, n-propanol and n-butanol. In the range

0–10^4 ppmv of the analytes we have grossly calculated the sensor response to n-butanol, which turns out to be 11.4×10^{-15} (A/ppmv) against 3.6×10^{-16} and 2×10^{-16} (A/ppmv) for n-propanol and ethanol. The sensor response to methanol is very small, about 0.2×10^{-16} (A/ppmv). An important feature of this material is its capability to discriminate alcohols with different aliphatic chains (see figure 6) [19].

We can calculate the sensitivity curves for our materials from their response curves by applying a derivative procedure reported in the literature [20]. The general definition of sensitivity for sensors nonlinear in character (N.L.T.C.), based on the output/input derivative, that applies the relation $\delta X/\delta M$ (X = output signal, M = measurand), can be simplified in those cases where the degree of nonlinearity can be neglected (L.T.C. with offset). On the other hand, the sensor response curve can be piecewise linearized; then many sensitivities can be defined, i.e. each one for each linear piece, but the interval to which the linearity applies should be specified (L.T.C. without offset sensitivity). Figures 7(a) and (b) illustrate a selected explicative case, which is that the curves represent the sensitivity of the nanostructured polymer P(PA/HEMA) on Cr and Au electrodes, calculated for the increase and decrease of n-butanol concentration; both curves show a similar sigmoidal behavior, slightly affected by the direction of the variation of the alcohol concentration.
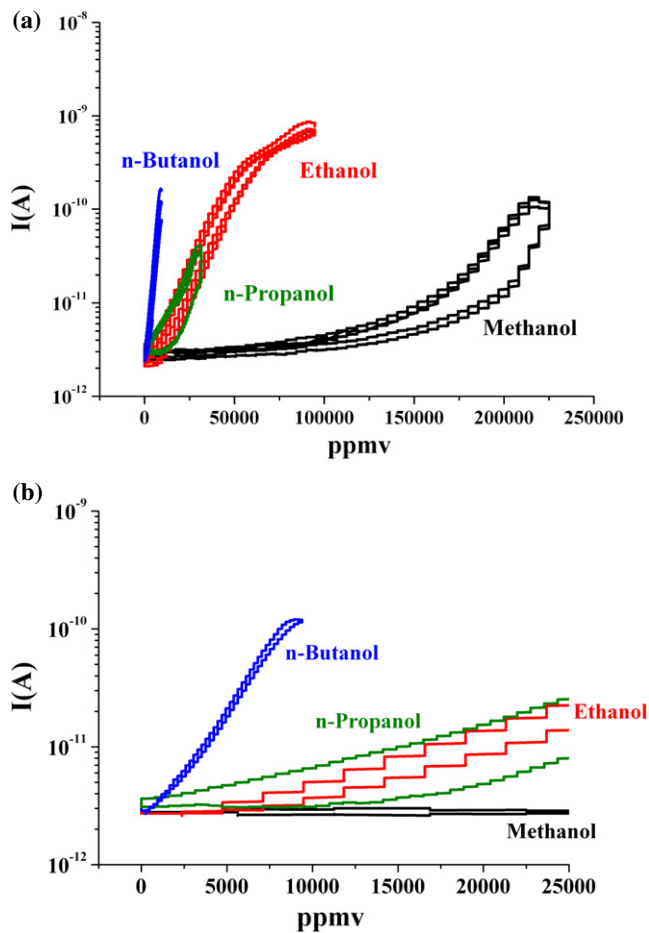
Figure 6. (a) Electrical responses of P(PA/HEMA) on Cr electrodes towards the chemicals under test, i.e. methanol, ethanol, n-propanol and n-butanol. (b) Magnification for low concentrations.

Figure 7. Sensitivity of nanostructured polymers on Au or Cr electrodes toward n-butanol.

4. Conclusion

Electrical measurements performed on nanostructured PPA and P(PA/HEMA) membranes show a sensory behavior of these polymers when exposed to different environments. Water, methanol, ethanol, n-propanol and n-butanol were tested in vapor phase and selectivity of the polymers towards water vapors and short chain alcohols was observed. In particular, nanostructured P(PA/HEMA) membranes were sensitive towards low relative humidity values (0–10%) while nanostructured PPA sensors appeared less efficient. The role of the metal electrodes on the response seems related to the chemical structure of the polymer rather than to the nanostructure. However, the film's nanostructure seems to play an important role in the improvement of sensor response in comparison with that of the same non-nanostructured materials. In particular, the P(PA/HEMA) polymer material has shown a better sensitivity to n-butanol. This property could be useful in applications such as automotive uses, where butanol is considered a promising high performance biological combustible that can moreover be used as a blended additive to diesel fuel in order to reduce soot emissions.
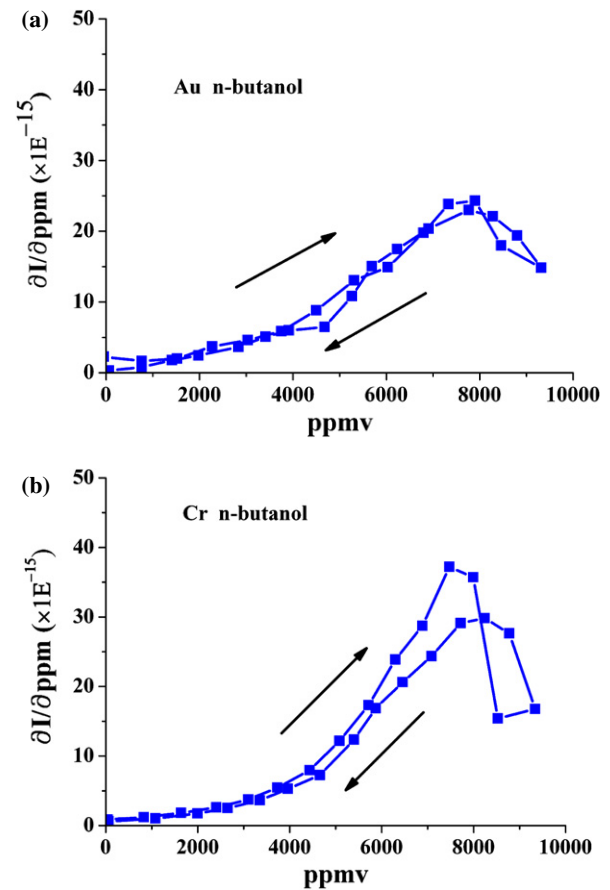
Acknowledgment

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