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Enhance of Sensitivity of Corrole Functionalized Polymeric Microspheres Coated Quartz Microbalances †

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Abstract: An innovative and efficient β-functionalization of [5,10,15-tris-(4-methylphenyl) corrolato]Cobalt derivatives introduced an acrolein substituent, which allowed the copolymerization with pure acrolein. The obtained hybrid microparticles have been used as sensing materials of quart microbalance gas sensors. The sensing properties have been tested by exposure to different volatile organic compounds chosen as model analytes. Results show an improved sensitivity of the hybrid microparticles respect to the individual constituents.

Keywords: quartz microbalance; gas sensors; corroles

1. Introduction

Porphyrins are macrocycles based on four pyrrole units interconnected via methine bridges. The basic structure is a template for the formation of complex molecules characterized by the addition of a metal ion at the core of the macrocycle and peripheral compounds. Such a molecule features remarkable properties in terms of binding, catalysis and charge transfer which are fully exploited in nature. On the other other hand, the porphyrin structure serves as a template for a family of molecules (called porphyrinoids) where the macrocycle is either shrinked or expanded. Porphyrinoids are endowed with remarkable gas sensing properties which take advantage of the molecular design flexibility [1]. Such features enabled, for instance, the development of quartz microbalance arrays for several applications, not least medical diagnosis [2], and optical sensors [3]. A typical defect of porphyrinoids based sensor is due to the tendency of these molecules to aggregate in solid films that becomes hardly permeable to gases. Years ago, we shown that this problem could be solved with a proper functionalization with alkyl chains of the molecular lateral positions [4]. Here, we introduce an alternative approach based on the copolymerization of a porphyrinoid functionalized with a proper functional group. For the scope, we considered a corrole functionalized with an acrolein group (full name and scheme in Figure 1). Respect to porphyrins, in corroles two pyrrole rings are directly linked. It results in a richer electron system than porphyrin, which contribute to confer to corrole distinct properties of catalytic activity, sensing, and photochemistry [5,6]. Acrolein-functionalized corroles have been added, at variable concentration, to the polymerization process of acrolein, which leads to the formation of polyacrolein (PA) microspheres. The so-obtained material was used to functionalize quartz microbalances that have been tested towards a number of model analytes.

Results show that, respect to pure corrole films, corrole-functionalized polyacrolein increases the sensor sensitivity. It offers a further degree of freedom to the design of gas sensor arrays.

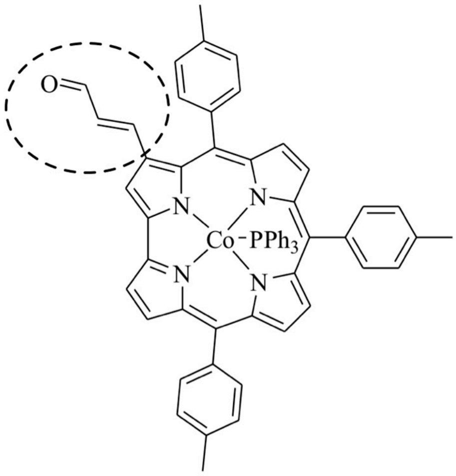

Figure 1. Scheme of the acrolein functionalized [5,10,15-tris-(4-methylphenyl)corrolato]Cobalt(III). Dotted circle evidences the acrolein group necessary to include the molecule in the polyacrolein.

2. Experimental

[5,10,15-tris-(4-methylphenyl)corrolato]Cobalt(III) was syntesized and added to the precursos solution of polyacrolein. Polyacrolein are known to assemble in microsphere. The addition of corroles does not change the morphology, as shown by SEM analysis in Figure 2, thus typical sub-micrometric particles are obtained.

Materials were prepared at two corrole to acrolein ratios: 1:250 and 1:1000. The materials were used to coat the surface of 20 MHz AT-cut quartz microbalances (QMB). For sake of comparison, sensors coated with the same amount of materials of pure corroles and pure polyacrolein were also prepared and tested.

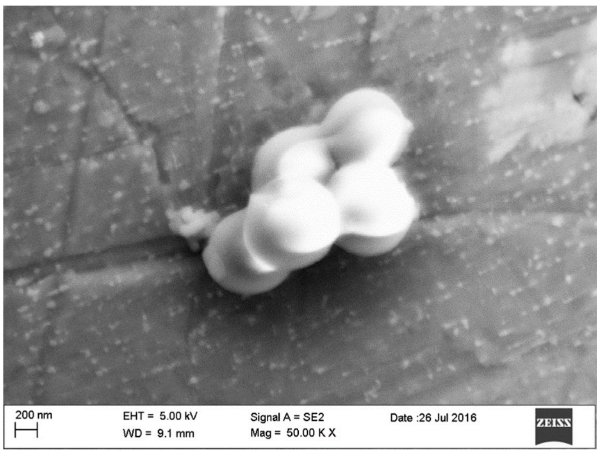

Figure 2. SEM image of corrole-polyacrolein. The diameter of each microsphere is of the order of few hundreds of nanometers.

3. Results and Discussion

The sensitivity of the sensors has been tested respect to four volatile compounds: benzene, ethanol, acetone, and triethylamine (TEA). These were chosen as model analyte with different chemical properties. The responses have been compared with those of QMB coated with either corrole or polyacrolein. Figure 3 shows the response isotherms. The largest signals are obtained by the microspheres functionalized with the largest amount of corrole (Corrole:PA 1:250). Since sensors were prepared with the same amount of material, the amount of corrole molecules and acrolein in the functionalized polymers is smaller respect to the sensors carrying either corrole or polyacrolein. Thus, the improved sensitivity cannot be merely ascribed to a quantitative effect; rather the increased interaction with airborne molecules is likely due to a more efficient arrangement of corroles along the polymer chain. Sensitivities were usually calculated as the slope of the response isotherm. The pattern of sensitivity is shown in Figure 4. All the four sensors exhibit their largest sensitivity to ethanol. This is not surprising because of the combined action of the cobalt ion in the corrole (which is a Lewis base) and the electric dipole of acrolein. It is important to observe that the largest increase of sensitivity in Corrole:PA 1:250 is observed for TEA, which among the tested compounds has the largest dispersion interaction. Due to this property, TEA can diffuse through the polymer to reach the corrole molecule.

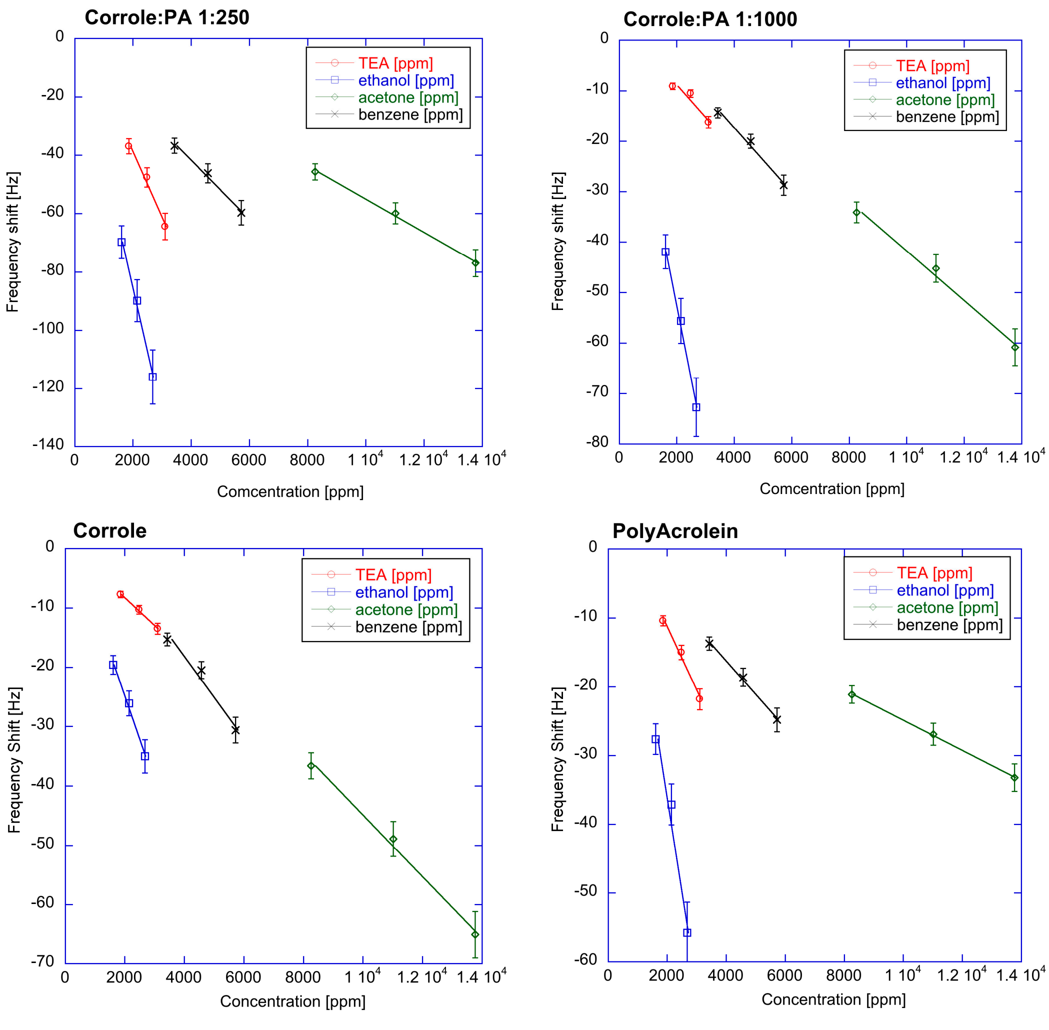

Figure 3. Response curve of four QMBs coated with corrole functionalized polyacrolein at two different acrolein:corrole ratios (1:250 and 1:1000), and two sensors coated with either corrole or polyacrolein.

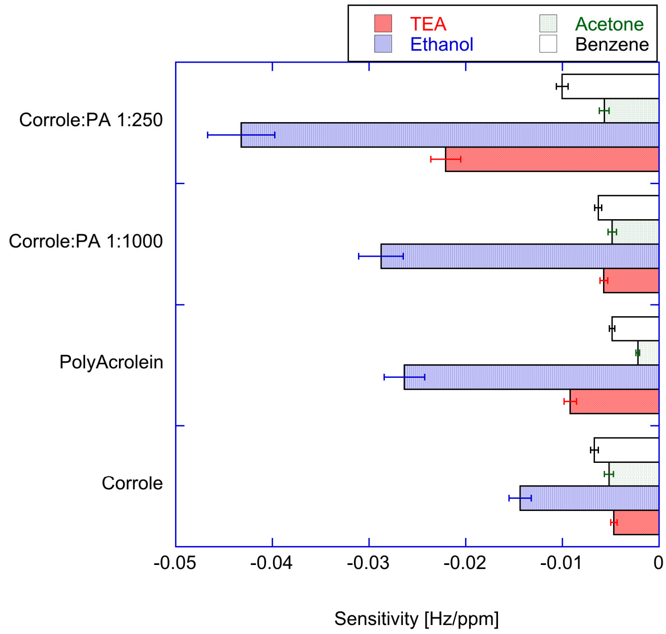

Figure 4. Sensitivity pattern of the four sensors. For the interpretation of these results it is important to consider the properties of the individual constituents. Corrole and polyacrolein show a large sensitivity to ethanol as expected by the Cobalt ion in corrole and electric dipole of acroleyn. TEA has the largest dispersion interaction and then it is better absorbed by the polymer, and π-π interaction may explain the favoured absorption of benzene in corrole. All these characters are preserved and amplified in the PA:corrole sensor with the largest ratio of corrole respect to acrolein. This behavior shows that Corrole:PA enables to get the better of both the individual constituents.

Conflicts of Interest: The authors declare no conflict of interest

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