

A novel multisensing optical approach based on a single phthalocyanine thin films to monitoring volatile organic compounds

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Abstract

This paper reports the use of optical transduction techniques to characterise solid state chemo-optical sensors prepared by Langmuir–Schäfer technique (LS) in thin film form based onto Cu(II) tris-(2,4-di-*t*-amylphenoxy)-(12-hydroxy-1,4,7,10-tetraoxadodecyl)-phthalocyanine macromolecules CuPcOH as active layers. The study consists in the UV–vis optical absorption monitoring of the active LS layers in the presence of specific five volatile organic compounds (VOCs) mixed in dry air in controlled atmosphere; in particular *tert*-butylamine, methanol, ethanol, hexane and ethyl acetate, all analytes of interests in the food quality control. The UV–vis spectra have been monitored by recording the dynamic variation in the integral of the absorbance curves in well defined spectral regions: 300–400 nm, 550–600 nm, 600–640 nm, 640–700 nm, covering the whole spectrum and centred around the typical absorption bands of phthalocyanine thin films. This simultaneous UV–vis four channel monitoring allowed to use only one active layer as sensing element where each selected spectral region generates independent sensors. The dependency of the above mentioned outputs towards the analytes has been discussed. A base optical characterisation of the investigated LS thin films has been performed.

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1. Introduction

In recent years, the solid state gas sensors demand for safety control requirements, environmental monitoring and food quality control has expanded enormously. In particular the detection of volatile organic compounds in low concentration has become of interest because they are widely used as ingredients house-hold products. These compounds vapourise at normal room temperature, sometimes causing adverse health effects. Moreover foods emit mainly low molecular weight alcohols and esters, but also amines and aldehydes are present.

To this purpose the sensing elements necessary to monitor specific gases or VOCs must demonstrate high selectivity feature. In the cases in which the sensing element not shows

the required selectivity, a development of an array configuration becomes indispensable. Consequently, a great interest on searching the solid state gas sensor with high sensitivity, stability and wide selectivity spectrum has been developed. In array configuration each sensing element must demonstrate a broad selectivity range towards various kinds of volatile organic compounds. But there is a research competition between the possible realisation of large number of sensors element disposed in array configuration or the tentative to modify the sensing technique in order to increase the selectivity of a specific sensitive material. In the first case the increasing of the number of sensing elements leads to increase the dimension of the system and the complexity of the sensing equipment. The second approach consists in the modification of the sensing technique, by minimising the use of the sensing material. Different transduction techniques are used for gases or VOCs detection such as electrical conductivity [1,2] mass transduction [3,4], surface acoustic

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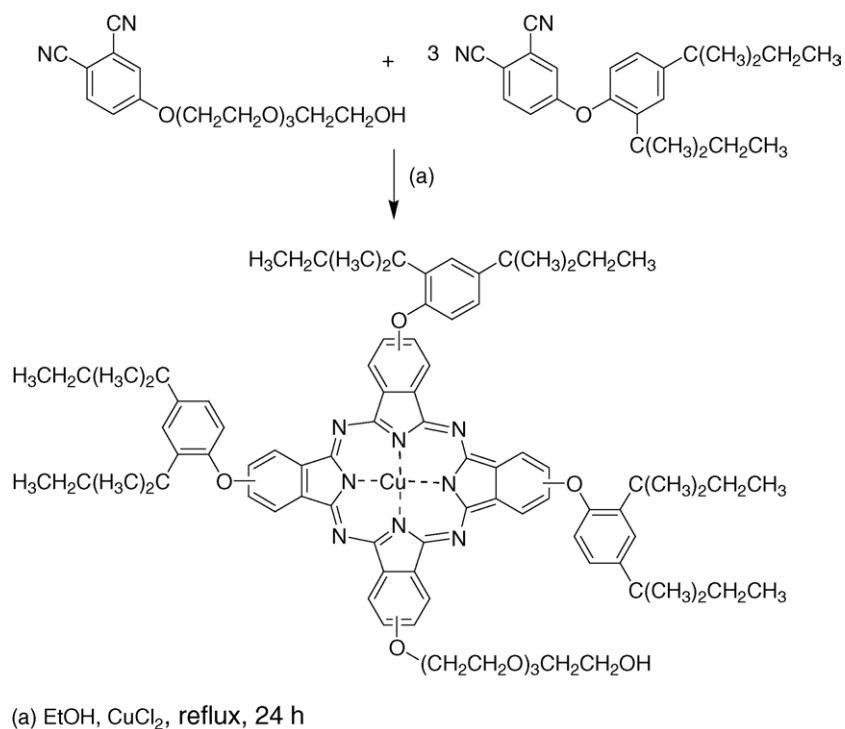


Fig. 1. Molecular structure of the CuPcOH.

wave [5] optical variation in the physical properties of the sensing elements [6]. In the last case optical detection of gases are based on the change in the optical properties of thin films (e.g. refractive index, extinction coefficient, thickness, absorption, etc.) due to the interaction of the sensing layer with the molecules of the gas. In this paper, optical sensing technique in which optical detection of gases was based on the change in the optical absorption properties of thin films of Cu(II) tris-(2,4-di-*t*-amylphenoxy)-(12-hydroxy-1,4,7,10-tetraoxadodecyl)-phthalocyanine macromolecules (Fig. 1) deposited by Langmuir–Schäfer technique has been used. Organic chemicals like metallophthalocyanines have been reported to be a prospective candidate as optical sensing element for volatile organic compounds detection [7]. Moreover, these chemicals were possible to prepare in the form of thin films using different chemical deposition techniques like casting, spin coating, Langmuir–Blodgett, or physical technique like thermal evaporation [8]. By considering that LS film based onto our phthalocyanine macrocycles shows typical Q and Soret absorption bands in the wavelength range between 300 and 700 nm our study involved the in situ monitoring of the absorption spectrum of these layers in the range from ultraviolet to near infrared and their variation due to thin sensing layer-vapours interaction. In particular, these absorption bands variations are dynamically analysed by considering four typical spectral regions: 300–400 nm, 550–600 nm, 600–640 nm, 640–700 nm corresponding to the specific phthalocyanine absorption peaks. In this way a single sensing layer, opportunely designed, can determine four independent sensors in an array configuration.

In our investigation we considered some VOCs which are of interest in food analysis. In particular those compounds with a well-known toxicity such as amines. Alcohols are also present in flower and fragrances related to many food products and involved in fats deterioration processes.

The responses obtained from our sensing layers are due to the exposition to different VOCs and can be used in a subsequent data processing step. To this purpose principal component analysis (PCA) has been performed to evaluate the discrimination power of the array towards some simple vapours. In particular sensing tests in controlled atmosphere at room temperature with the active layer successively exposed to a successive exposition of vapours of *tert*-butylamine, methanol, ethanol, hexane and ethyl acetate have been performed and discussed.

2. Experimental

2.1. Reagents and instruments

All the starting materials were purchased from Aldrich Chemical Co. and used as received. Silica gel (Merck) was used for the chromatographic separations. Solvents were dried and distilled under N₂ atmosphere. FT-IR spectra were recorded on a JASCO FT-IR-430 spectrometer. UV–vis spectra of the solution and thin LS films were recorded by using a Varian Cary 500 scan UV–vis spectrophotometer. ¹H NMR spectra were recorded on a Bruker AC-400 at room temperature in CDCl₃ and internally referenced to CHCl₃. GC/MS

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