Sensors and Actuators B 230 (2016) 320–329

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Phthalocyanines based QCM sensors for aromatic hydrocarbons monitoring: Role of metal atoms and substituents on response to toluene

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ARTICLE INFO

Article history:
Received 7 November 2015
Received in revised form 4 February 2016
Accepted 9 February 2016
Available online 11 February 2016

Keywords:
Phthalocyanines
QCM transducer
Air quality control
Non-covalent interactions
Organic electronics
Thin film

ABSTRACT

The sensing properties of various metallophthalocyanines layered on Quartz Crystal Microbalance (QCM) transducers towards toluene vapor were investigated. Structural and morphological properties of thermally evaporated thin films of substituted and unsubstituted phthalocyanines were firstly characterized by Infrared spectroscopy, X-ray Diffraction and Scanning Electron Microscopy. The sensing characteristics were then determined from QCM responses to toluene at room temperature and correlated to physical and chemical properties of thin films. Effects of molecular composition of phthalocyanine, especially the nature of metal atom in the central cavity and peripheral grafted substituents, on sensor metrological characteristics were established. No significant effect because of change of the central metal atom (Cu, Zn, Fe, Co) in monomeric phthalocyanines was observed on toluene sensitivity. In contrast, strong effects of substituents particularly *tert*-butyl group at the periphery of the phthalocyanine ring on sensor response were highlighted. The sensing behavior of metallophthalocyanines towards toluene has been interpreted in correlation with the chemical nature of the materials (nature of metal atom and peripheral grafting groups), the physical properties of the sensitive films (structure, morphology and thickness) and the involved molecular interactions forces.

1. Introduction

Phthalocyanines are organic molecular materials [1,2] which have been extensively studied since their discovery in early 20th century in the diverse domain of organic electronics. The electrical, optical and chemical properties emanating from the atomic arrangements and electronic distribution within the molecules have positioned these materials in multifaceted research dimensions. Metal-free phthalocyanine is a planar molecule because of continuous conjugation of 18 π-electrons within it. It consists of a central cavity and chemically active sites at its periphery where a lot of molecular engineering can be performed to suit the need of respective applications. The two central hydrogen atoms can be replaced by more than 70 metal atoms [3] and a variety of substituents can be incorporated, both at the periphery and at the axial positions of the molecule. Therefore a large number of metallophthalocyanines can be synthesized as reported in the literature [4–8]. The flexibility of this molecule to manipulate its structure imparts tremendous variations in optical and electrical properties [9–14]. The electronic properties of metallophthalocyanines have been a much debated topic. These materials can behave like an organic semiconductor [6]. The type of which is decided by the nature of substituent/substituents attached at the peripheral sites and metal atom present in the central cavity [15,16]. Considerable efforts have been made to understand the structure-properties relationship in order to find their potential applications in electronic devices and particularly in the field of chemical sensors. The semiconducting nature, presence of delocalized π-electrons in the macrocycle, aromatic character and intense optical absorption make them an appropriate sensing material in different transducing mode [17–20]. It includes resistive [21], optical [22] as well as acoustic sensors [23]. A number of pollutant species were targeted using phthalocyanines based gas sensors. It included volatile organic compounds (VOCs) (benzene, toluene, xylenes,

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http://dx.doi.org/10.1016/j.snb.2016.02.032

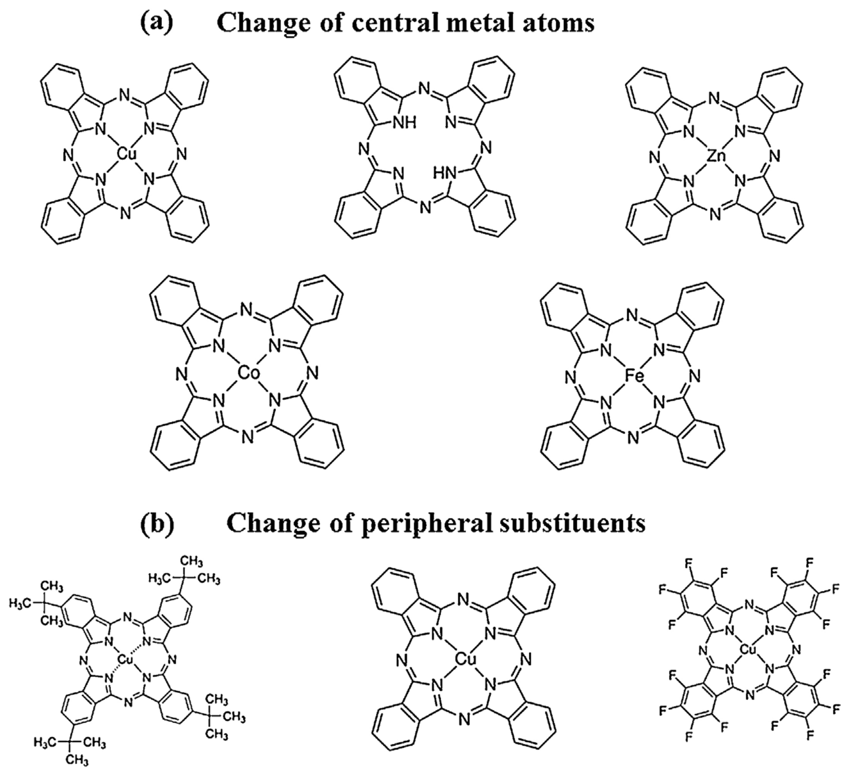

Fig. 1. Representation of studied phthalocyanines emphasizing (a) phthalocyanines with different metal atom and (b) phthalocyanines with different substituents.

chloroform, ethanol, acetone, etc.) [23], nitrogen dioxide [24], ozone [25], hydrogen sulfide [26] and many others.

In this article, we restrict our investigations on phthalocyanines as a sensitive material of gas sensors particularly devoted for toluene vapor detection. Toluene is a VOC, which has become a serious health hazard in recent decades [27,28]. Based on adverse health consequences linked to toluene exposure many national/international health care and environmental protection agencies have given emission guidelines in different working environments. Some of these recommendations are also implemented as legislations. Taking into account stringent emission guidelines/legislations, continuous monitoring of toluene vapor becomes an important requirement. Conventional methods of detection are mainly based on automatic gas chromatograph [29,30] using gas analyzers in fixed air quality stations. These methods are although sensitive and selective but lack of mobility, long analysis time and high cost involved limit their applications in wide-scale and real-time detection. A gas microsensor system can be a viable solution which can address the limitations of conventional protocols of detection. Considering the presence of delocalized π-electrons in phthalocyanines materials and the aromatic nature of toluene molecule, they can interact to each other via π–π interactions [31–35]. To measure the interaction between phthalocyanines and toluene we need a measurement system in which detector output changes with the strength and extent of interactions. Quartz Crystal Microbalance (QCM) is one of the widely used transducer which can serve the above mentioned purpose. It works on the principle that mass variation on the transducer active surface consecutively to gas adsorption leads to change in crystal resonance frequency according to the Sauerbrey's equation [36]. Phthalocyanines based QCM sensors were used in past for detection of VOCs including toluene [37,38]. These studies established sensitivity of phthalocyanines towards benzenoid gas analytes. The variations of molecular parameters especially the central metal atom and substituents can be a crucial area which can affect the sensitivity towards a targeted gas analytes. A comparative gas sensing studies of different metallo- and metal-free phthalocyanines based chemoresistors were reported by Ref. [39]. They investigated the variations in sensitivity towards electron donor organic vapor because of change of metal atoms by correlating thermodynamic parameters. The comparative gas sensing studies of metallo- and metal-free as well as substituted and unsubstituted phthalocyanines based QCM sensors towards aromatic hydrocarbons are still unexplored.

The aim of this article is to highlight the sensitivity of phthalocyanines based QCM sensors towards toluene and to understand the effects of change of molecular parameters of sensing material on the gas interaction phenomenon. Our investigation is broadly divided into two parts; (a) study of effects of metal atom in the central cavity of phthalocyanine on toluene sensitivity and (b) investigation on the role of peripheral substituents in phthalocyanines on their sensing behavior with toluene. Variations of these parameters in a phthalocyanine macrocycle are depicted in Fig. 1. Change in QCM sensor response to toluene of different phthalocyanines materials have been correlated to variation in molecular organizations in the sensing layers and morphologies of the surface. The variations in gas/material interaction induced by the change in central metal atoms and peripheral ligands in phthalocyanines have been further interpreted on the basis of non-covalent interaction forces.

Table 1
Lattice parameters of CuPc and ZnPc semi-crystalline layer.

Materials	a(A°)	b(A°)	c(A°)	β(°)
CuPc	19.43	4.70	14.79	120.37
ZnPc	19.22	4.87	14.52	120.03