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Study of interaction mechanism of metal phthalocyanines dispersed sol-gel glasses with chemical vapours

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ABSTRACT

In the present study, we have dispersed copper phthalocyanine, nickel phthalocyanine and aluminium phthalocyanine hydroxide in sol-gel glasses. These have been exposed to methanol, benzene, diethylamine and bromine vapours. Interaction mechanism of phthalocyanines with these vapours has been studied by electrical and spectroscopic techniques. The variations in the sensitivities of these MPCs dispersed glasses have been explained on the basis of primary and secondary charge transfer mechanisms between the adsorbed chemical vapours and MPCs. The structural and optical behaviors of these dispersed glasses have been analyzed using X-ray diffraction; UV-vis, Fourier transform infrared spectroscopy and field-emission scanning electron microscopy analysis.

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1. Introduction

The management of toxic elements in the environment has led to the need of materials that are selective, sensitive, reversible and reliable in terms of their sensing properties. Phthalocyanines (Pcs) are organometallic compounds that exhibit a unique combination of chemical, electrical and optical properties which make them suitable as gas sensors [1], industrial colorants [2], photosensitizers [3], and catalysis [5]. We also find their applications in molecular electronics and medicine [4,5]. Phthalocyanines and their metal analogues are considered as preferred materials for gas sensing because of their increased selectivity which arises due to their flexibility and the ease of their modification [6]. This is unlike the case of oxide materials which lack selectivity [7,8]. Apart from this, their increased thermal stability makes them suitable even at elevated temperatures (400 °C–500 °C) for sensing applications [9]. Pcs are synthetic tetrapyrrolic compounds consisting of four isoindole units linked together by nitrogen atoms. Most of the elements are able to coordinate to the Pc macrocycle. Furthermore, the central metal of MPC can take additional ligands and it can be easily functionalized with various substituent groups (Fig. 1). Therefore, by changing these parameters, Pcs can be made selective to different types of gaseous species [6,9]. MPCs (M = Pb, Fe, Co,

Ni, Cu, Zn and others) generally exhibit increase in the current on exposure to strongly oxidizing gases; the sensor films are partially oxidized, forming charge transfer complexes which inject holes and hence increase in the majority charge carriers which results in the increase of the conductivity of the film [10–15]. Similarly reducing gases have the opposite effect [15–19]. Therefore, these materials have been exploited in gas sensing applications since electronic properties of metal phthalocyanines (MPCs) thin films are affected by the adsorption of oxidation or reducing gas [6].

Phthalocyanines have hydrophobic nature; they are insoluble in water and various polar solvents, therefore, the most common method of deposition of thin films of MPCs is by thermal evaporation method [20]. But they can be made soluble in organic solvents by functionalizing them with various substituent groups or adding some ligands to the central metal atom of the Pc ring [21]. Accordingly, they can be prepared through chemical methods in various forms, like sol-gel glasses, powder, thin films and many more. The advantage of preparing the material in the sol-gel glass form for gas sensing purpose lies in the porous structure of the glass. Their porous structure is responsible for uniform and easy diffusion of the analyte gas or chemical vapour species into the target sample which leads to an efficient mechanism of chemical interaction [22–24].

MPCs containing metal centers such as iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) are widely used in catalysis, sensor applications and molecular electronics studies [25,26]. The advantage of Cu to be used in MPCs is due to its antiviral

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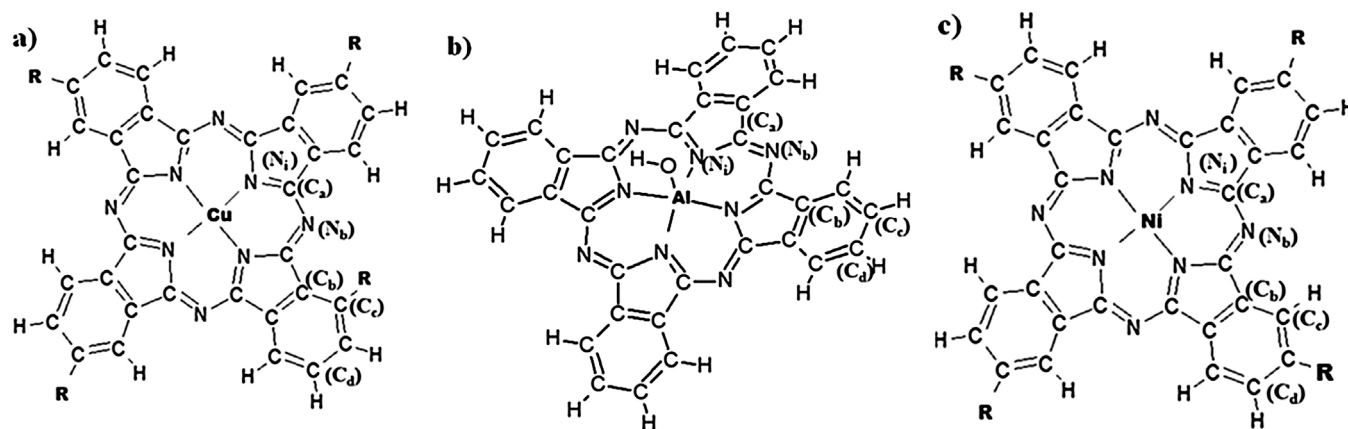


Fig. 1. (a–c). Structure of Metal Phthalocyanines with functionalized groups (Tetrasulfonic acid tetrasodium salt; 4 groups of R as O_2S-O_2Na in case of CuPcS and NiPcS and H in case of AlPcOH).

and virucidal activity, low toxicity, low cost and high thermal stability [27]. The studies on temperature-sensitive chemical cells made of nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPcS) in aqueous medium and copper (II) phthalocyanine-tetrasulfonic acid tetrasodium salt (CuPcS) have been reported to develop an enhanced temperature sensor with higher sensitivity and consistent response in the temperature regime from room temperature to below 100°C [27–29]. Films of MPcs functionalized substituent groups have been found to have relatively high values of the mobilities of charge carriers, which are two orders of magnitude higher than the values of the mobilities of charge carriers in the case of unsubstituted MPcs films [30]. Therefore, these materials have advantage over unsubstituted MPcs in improving gas sensing applications. Adsorption of oxidizing gas molecules on the surface of organic films with positive majority charge carriers (holes) that is *p*-type materials, such as films of substituted and unsubstituted metal phthalocyanines, changes the electrical conductivity of the films [29,30]. The conductivity of the normal *p*-type phthalocyanine complexes has been found to decrease under a nitrogen gas purge as dioxygen dopant is lost from the film, whereas the *n*-type Cu(II) perfluorophthalocyanine complex shows an increase in current under nitrogen purge [31]. The increase is due to the adsorbed dioxygen that acts as a counterdopant and scavenge electron carriers to decrease current. The adsorption of reducing gas molecules, in particular, ammonia, can lead to a decrease in the electrical conductivity provided by the motion of positive charge carriers in an organic film [32]. In composite materials based on CuPc and SnO_2 nanoparticles, the adsorption of ammonia at a concentration of 10^{-4} ppm of the saturated vapour concentration resulted in a 1000-fold increase of the electrical conductivity [15]. Adsorption of sodium salt of sulfonated aluminium phthalocyanine hydroxide on metal oxide layers shows good stability and sensitivity to humidity and ambient gases [33]. Aluminium phthalocyanine also enhances the catalytic properties especially when modified with some functionalized groups or adding hydroxyl (OH) group to it [34].

In the present work, we have prepared the sol-gel glasses dispersed with CuPcS, NiPcS and aluminium phthalocyanine hydroxide (AlPcOH). In porous sol-gel glass, the uniform adsorption allows effective chemical interaction between the target sample and the analyte gaseous species. The principle of gas sensors relies on the fact that when the chemical vapour is adsorbed onto the surface of the sample, it undergoes some physical changes such as mass, temperature, conductivity, polarization or optical properties which depend on the molecular properties of the materials like size, polarity, reactivity and affinity. These properties are further

exploited for their various applications like photovoltaic, sensing or catalysis applications and many more. Therefore, in the present study, we have dispersed CuPcS, NiPcS and AlPcOH in sol-gel glass to achieve uniform and effective adsorption of chemical vapours on them. Electrical conductivity is taken as a detection parameter to study the sensing mechanism with these vapours.

The variations observed in their electronic transition levels as well as molecular vibrational levels after vapours exposure are studied using ultraviolet-visible (UV-vis), Fourier transform infrared (FTIR) and Raman spectroscopies, respectively.

2. Experimental details

2.1. Materials used

Copper phthalocyanine 3, 4', 4'', 4''' tetra-sulfonic acid tetrasodium salt (dye content 85%), nickel phthalocyanine tetrasulfonic acid tetrasodium salts (dye content 85%) and aluminium phthalocyanine hydroxide powder (dye content 85%) powders were purchased from Sigma Aldrich. To form the silicate solution, tetraethylorthosilicate (TEOS), ethanol and concentrated HCl were purchased from Sigma Aldrich. The MPcs solutions were prepared in de-ionized distilled water which was used throughout the experiment. These chemicals were used as purchased without further purification. All other chemicals used were of analytical grade.

2.2. Preparation of CuPcS and NiPcS sol-gel glasses

Tetraethylorthosilicate was used as a silicate source for the preparation of MPcs dispersed sol-gel glasses. Ethanol and TEOS were used in 50:50 ratios so as to avoid any sort of aggregation [35,36]. $50\ \mu\text{l}$ of HCl and 3 ml distilled water were added as supporting dopants to enhance the solubility of the various solvents. For the preparation of CuPcS and NiPcS dispersed glasses, CuPcS and NiPcS powders (each 5 mg) respectively, were dissolved in 5 ml of distilled water to obtain their solutions. The mass content of CuPcS and NiPcS powders were kept same. Equal volumes of ethanol and TEOS (15 ml) were added into a beaker and 3 ml of distilled water with $50\ \mu\text{l}$ of HCl were added as supporting dopants. The obtained solution was stirred for around 3 h at room temperature to obtain a clear and transparent silicate solution. After 3 h the respective MPcs salt solutions were added into this solution which was then heated at around 340 K and stirred till the formation of the gel after about 2–3 h. Thereafter the obtained gels were dried for about 12 h resulting in the MPcs dispersed sol-gel glasses.

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