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Polymerized linseed oil coated quartz crystal microbalance for the detection of volatile organic vapours

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ABSTRACT

Quartz crystal microbalance (QCM) sensors are developed from polymerized linseed oil and used for the detection of volatile organic compounds (VOCs) such as p-cresol, o-xylene, benzene, and toluene. The polymer film on QCM surface is synthesized from the free radical polymerization of linseed oil in chloroform using benzoyl peroxide as initiator by dip coating method. The sensitivity, stability and selectivity of the sensors are measured by exposing the QCM surface to vapours. The synthesis of films are optimized and is found to have maximum adsorption of vapours when it is polymerized with 1.7% (w/v) of benzoyl peroxide. Among these four types of vapours, the maximum sensitivity is found with p-cresol and frequency shift of 110 Hz is obtained for 250 ppm of p-cresol vapour in nitrogen atmosphere. The sensor responses of concentration ranges from 5 to 250 ppm are found to be linear. The structure of the polymeric films is confirmed by FTIR analysis. Surface morphologies of the films before and after absorption are studied using AFM. The sensors are reactivated by releasing the adsorbed vapour by passing dry nitrogen gas. The sensing responses of VOC are observed to be substantial and reproducible.

1. Introduction

The volatile organic compounds (VOCs) are important area of studies for monitoring the status of pollutions in environment, because these pollutants enter water, soil, atmosphere and are very much harmful for the human health [1–4]. It is due to the carcinogenic, teratogenetic or mutagenic behavior of VOCs [5–7]. The VOCs like benzene, toluene and xylene are produced in our daily lives from home and personal care products, building materials and cosmetics. Cresols are widely spread in nature and occur in many plants, petroleum, coal tar, crude oil and volcanic eruptions. They are emitted from municipal incinerators, combustion of coal and wood, vehicle exhaust, oil refineries and cigarette smokes [8,9]. For this reason, development of sensors for the detection of VOCs have attracted special attention due to their potential applications in the fields of environmental and health monitoring [10]. Amongst sensors, quartz crystal microbalance (QCM) is very sensitive system for detection of low concentration of organic volatiles. The QCM is a piezoelectric material which consists of a thin plate of quartz crystal coated with silver electrode on both sides. It has a unique resonance frequency and it converts surface acoustic waves to electric signals. When the chemically sensitive thin film on QCM surface adsorbs specific molecules, the mass of the film increases which causes the decrease in the frequency of the QCM [11]. This change in frequency can be detected with the help of a frequency counter when the acoustic wave is converted to an electric signal.

Literature survey reveals that thin or thick film of polymer or its composites are useful in QCM sensor. Polymethylmethacrylate (PMMA) polymer film is used to measure the water vapour concentration [12]. Polysiloxane sensing film is more sensitive towards the detection of dimethyl methyl phosphonate (DMMP) [13]. The non-conductive polymers such as polyvinyl alcohol (PVA) and polyacrylic acid (PAA) films on QCMs are sensitive to organophosphorus pesticide *o,o*-dimethyl-*o*-2,2-dichlorovinyl phosphate (DDVP) [14]. Polyethylene imine (PEI), the polymeric layer with increasing surface area by Al_2O_3 porous film on QCM sensor is developed for the detection of methylmercaptan (CH_3SH) [15]. The QCM with polyvinylidene fluoride (PVDF) as sensing film is used for the detection of dimethyl methylphosphonate (DMMP) vapour which is a nerve agent [16]. QCM based sensor made up of toluene and p-xylene molecular imprinted polymers films (MIPs), composed of polymethylmethacrylate (MMA) co-divinylbenzene have been developed for the detection of toluene and p-xylene [17]. The cross-linked poly(styrene-co-chloromethylstyrene) reacts with morpholine to generate the morpholine-functional cross-linked copolymer which is used for the detection of NO_2 concentrations in air [18]. The electrospun nanofibers, composed of cross-linkable polyacrylic acid (PAA) and polyvinyl alcohol (PVA) are deposited on

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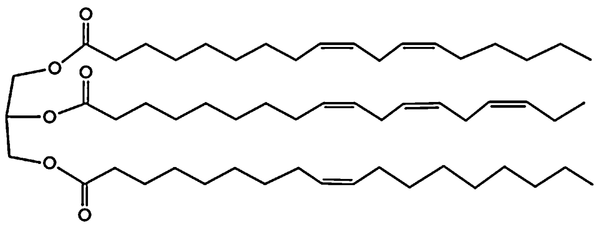

Fig. 1. The chemical structure of linseed oil.

QCM by electro spinning and is used for detection of NH_3 [19]. For the detection of amine odors, QCM sensor is developed by employing an ultrathin film formed by the alternate adsorption of TiO_2 and polyacrylic acid (PAA) [20]. For the rapid detection of formaldehyde electrospun nanoporous polystyrene fibers are deposited on polyethyleneimine (PEI)-functionalized QCM [21]. The conducting polymer composites such as PVC and PMMA with active functional groups and SPEs are used to detect volatile gases [22,23] and electro polymerizing pyrrole in a cross-linked matrix is found to be sensitive towards NH_3 [24]. The gas sensing properties of polypyrrole by exposing polypyrrole impregnated filter paper to ammonia vapour is investigated by Nylander et al. [25]. It is noticed that PANI–PMMA composite coatings are sensitive to very low concentrations of NH_3 gas even less than 10 ppm .The synthesized acrylic acid doped polyaniline is sensitive to ammonia vapour over a broad range of concentrations of 1–600 ppm [26]. Electro active nanocomposite ultra thin films of polyaniline (PAN) and isopolymolybdic acid (PMA) are used for detection of NH_3 and NO_2 gases [27]. Linseed oil coated electrodes have been used in the detectors of Large Hydron Collider and similar sophisticated equipments to protect the electrodes from moisture adsorption [28,29].

It is well known in paint formulation that the linseed oil and similar unsaturated oils can form solid films in presence of drying agents like organic salts of Mn and Co [30,31] in presence of O_2 from air through the cross linking between glycerides of unsaturated fatty acids. The chemical structure of the linseed oil is shown in Fig. 1. The major constituents of linseed oil are α-linolenic acid (60%), linoleic acid (29%), and oleic acid (27%). Linseed oil, which contains 60% α-linolenic acid, is an example of nonconjugated oil and it is rich in polyunsaturated fatty acids. These polyunsaturated fatty acids contain double bonds which facilitate the polymerization using free radical [32].

As mentioned above, there are some studies for detections of organic vapours using polymer films in QCM, but the polymerized linseed oil as an adsorbent is not reported earlier. In the present study, we have taken polymerized linseed oil as a new adsorbent for the detection of VOCs by using QCM. The polymerized linseed oil is used as adsorbing film of QCM for the detection of vapours of p-cresol, o-xylene, benzene and toluene. Benzoyl peroxide is used as an initiator for polymerization to avoid the dependence of polymerization on air and inorganic catalyst. The coated film of linseed oil by dip dry method is heated to get a stable cross linked film in presence of organic peroxide under argon atmosphere. The sorption mechanism, sensitivity at different concentration of analyte and the reproducibility of the sensor response are discussed in the text.

2. Experimental

2.1. Materials

Benzene, toluene, o-xylene, p-cresol, chloroform and benzoyl peroxide are procured from E. Merck, India and linseed oil is procured from Sigma–Aldrich. All solvents and reagents of analytical grade are used as such without any further purification. AT-cut 10 MHz quartz crystals with silver electrodes on both sides are procured from BEL, India.

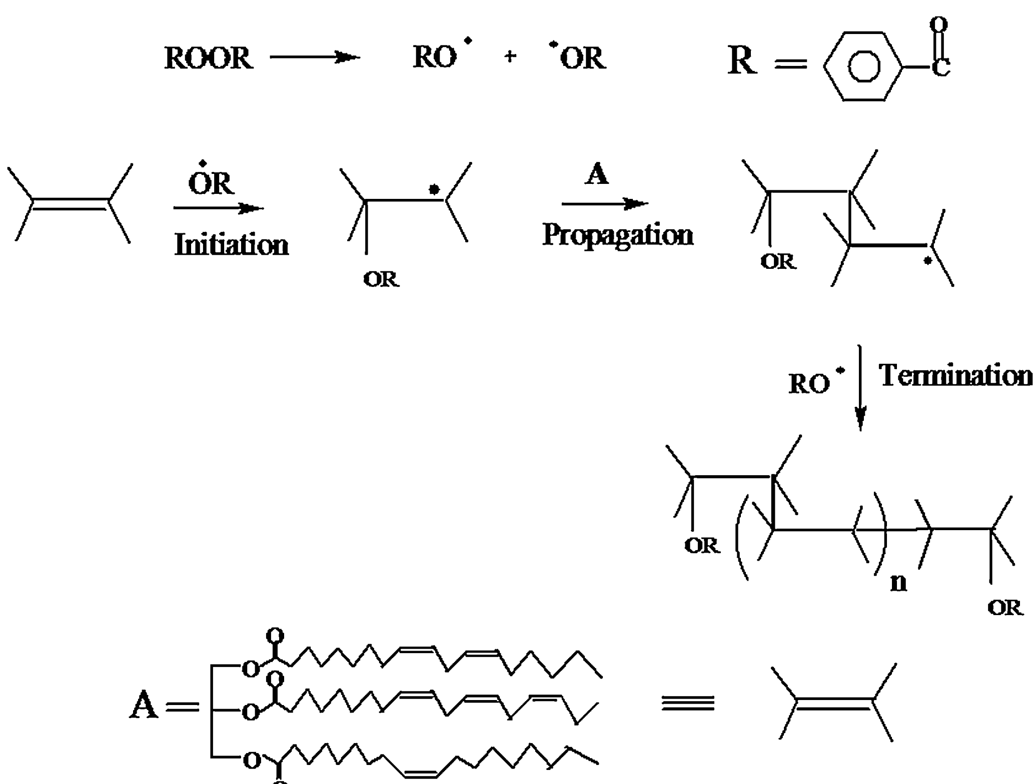

Fig. 2. Reaction mechanism of polymerization of linseed oil.