





Research paper

High carrier mobility and environmentally stable microporous zeolite imidazolate framework (ZIF-67): A field-effect transistor (FET) approach

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Highlights

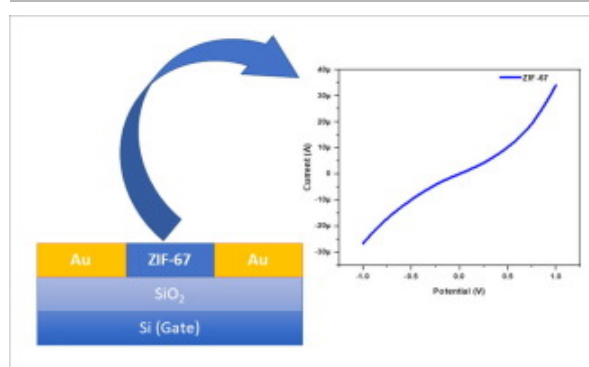
- The Zeolite Imidazolate Framework (ZIF-67) was successfully synthesized.
- FET based on ZIF-67 exhibited p-type behaviour with highest hole mobility $\sim 0.85 \text{ cm}^2/\text{Vs}$ and current Ion/off ratio 10^2 .
- ZIF-67 exhibited excellent environmental stability up to 40 days.

Abstract

The present investigation dealt with the synthesis of ZIF-67 and its exploration as an effective channel material for the applications based on Field-Effect Transistor (FET). The ZIF-67 was characterized by the spectroscopic, structural, morphological, thermogravimetric analyzer (TGA), and Brunauer–Emmett–Teller (BET) techniques. The transfer characteristics of ZIF-67 exhibits the p-

type performance with hole mobility of $\sim 0.85 \text{ cm}^2/\text{Vs}$ and the current $I_{\text{on/off}}$ ratio 10^2 . The fabricated FET device based on micro porous ZIF-67 exhibited excellent environmental stability up to 40 days.

Graphical abstract



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Introduction

Since the discovery of metal–organic frameworks (MOFs), it has acquired significant study in potential applications such as heterogeneous catalysis and gas storage/separation [1], [2], [3], [4], [5], [6]. Zeolitic imidazolate frameworks (ZIFs) are categorized under a distinct group of hybrid organic/inorganic materials described as metal–organic frameworks (MOFs), which is having similar topologies like zeolites with exciting properties [7]. The ZIF-67 manifests a large surface area, exceptional adsorption affinities, comparatively eminent chemical/thermal stability and permanent porosity, and hence becoming a functional material for many industrial applications. Vital improvement has been executed in recent years for developing the ZIFs into membranes, liquid separation (pervaporation), and functional devices [8], [9], [10], [11], [12], [13], [14]. The crystalline characteristics of porous material are divided into three categories based on pore opening: (i) microporous (0.2–20nm), (ii) mesoporous (2–50nm), and (iii) macroporous (50–1000nm) [15]. Phan et al. reported that the zeolites could be recognized as the angle made by the M–Im–M fragment (145°) (where M denotes Zn or Co, and Im signifies imidazolate) which are related to that of bridging angle in Si—O—Si [11].

Stephen et al. successfully represented the electrochemical applications for ZIF-coated electrodes and observed the areal capacitance of $0.01045 \text{ F cm}^{-2}$ at 0.01 V/s for additive-free Co based ZIF-67 coated electrodes [12]. The interdigitated electrode coated ZIFs was successfully applied by Zhang group in resistive sensor array. It was studied in previous report, the ZIF-67 was applied to sense formaldehyde vapor at lower concentrations (5ppm) [13]. Daniel et al. synthesized ZIF-8/ZIF-67 to

Typesetting math: 100% tivity towards the hydrogen detection. The sensor can detect low

concentrations up to 10 ppm of hydrogen [16]. Li et al. synthesized the cobalt-based ZIF-67 and explored to the elimination of poisonous Cr (VI) from an aqueous medium. The Cr (VI) was quantified at low concentrations i.e. 6 ppm within 20 min [17]. Zhen et al. prepared thin film electrodes of ZIF-8 and ZIF-67 by direct drop-casted the mixture over a copper foil. Further, these electrodes were explored to electrochemically investigate the lithium-ion battery applications [18]. The organic field-effect transistors based on MOFs materials has been developed owing to its high potential in electronics, optoelectronics, and solar cell applications [19], [20], [21]. It is reported, the Co^{2+} based ZIFs materials exhibit lower resistance i.e. 1000 times than that of Zn^{2+} in the subcategory of the metal-organic framework [22]. This material's energy bandgap comes under the semiconducting region, i.e., typically 1–2 eV, which will be useful for electronics applications in the future [23]. As a relatively unusual expansion of the extensively studied metal-organic frameworks, there has recently been a growing interest in studying ZIFs.

A unique category of microporous conducting materials compels us to fabricate a field-effect transistor (FET) device employing a ZIF-67 as the functional channel material. There are few porous MOF materials capable of showing a FET behaviour with low charge carrier mobility reported in the literature [24], [25], [26], [27], [28]. The detailed comparison is shown in results and discussion section (Table 1). The FET fabricated based on ZIF-67 exhibits the typical p-type behaviour with carrier mobility value of $\sim 0.85 \text{ cm}^2 \text{ V/s}$, which may possible due to the positive zeta potential of ZIF-67 [29], [30]. As per our knowledge, this is the first attempt of ZIF-67 based FET. This work's avenues may provide a practical path towards the remarkably new applications of conducting zeolites in the future.

Section snippets

Materials

The cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methylimidazole of high purity grades ($\geq 99\%$) was procured from Sigma Aldrich. The methanol was procured from Alfa Aesar. All these materials utilized without additional purification and used for the synthesis purpose....

Synthesis of ZIF-67

The ZIF-67 metal-organic frameworks based on Co(II) were synthesized under an ambient environment. The Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (0.87 g) was added into 30 mL methanol (CH_3OH) to produce a final solution....

Powder X-Ray diffraction (PXRD)

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The structural information of synthesized ZIF-67 was collected with Bruker (D8 Advance, Germany) at 40kV and 40mA using Cu K α radiation ($\lambda=1.54059\text{\AA}$). The diffraction pattern was measured in the 2θ range of 5° – 40° . All diffraction peaks correspond to ZIF-67 were well matches with the simulated as well as the previously reported results [35]. The average crystallite size of ZIF-67 was determined by applying Debye–Scherrer’s equation, as defined in the Eq. (2) [32], [36], [37]. $D = \frac{0.9\lambda}{\beta \cos\theta} \dots$

Conclusions

In summary, we have fabricated field-effect transistor based on microporous ZIF-67 MOFs by drop casting it between two gold microelectrodes. The fabricated devices showed remarkably good mobility in the category of ZIFs. The ZIF-67 exhibited the typical p-type behaviour with hole mobility of $\sim 0.85\text{cm}^2/\text{Vs}$ and current $I_{\text{on/off}}$ ratio 10^2 amongst the subcategory of metal–organic frameworks materials. The present research directed towards the new field of investigation as the use of a ZIF-67 as a...

CRediT authorship contribution statement

Pasha W. Sayyad: Project administration, Investigation, Methodology, Software, Writing - original draft, Data curation, Conceptualization. **Aafiya A. Farooqui:** Writing - review & editing, Visualization, Data curation, Validation. **Nikesh N. Ingle:** Visualization, Data curation. **Theeazen Al-Gahouari:** Formal analysis. **Gajanan A. Bodkhe:** Software. **Manasi M. Mahadik:** Formal analysis. **Sumedh M. Shirsat:** Formal analysis. **Mahendra D. Shirsat:** Conceptualization, Supervision, Writing - review & editing,...

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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...To identify the structures of the prepared ZIF-67 and ZIF-67@DTMS NPs, XRD analysis was also conducted. As presented in Fig. 2(d), the diffraction pattern of ZIF-67 NPs well matches the simulated diffraction pattern of ZIF-67 single crystal reported in the literature [40–42], which confirms the successful preparation of ZIF-67 NPs. The characteristic peaks of ZIF-67 NPs are all narrow peaks, and no other peaks, indicating the high purity and complete crystal structure of the synthesized ZIF-67 NPs....

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...For DSC curves of two materials shown in Fig. 1d, two obviously endothermic peaks appeared, which were in good correlation to the two major weight loss stages shown above (Fig. 1c). The heat related to the decomposition of N@ZIF-67 was higher than that of ZIF-67, because the former had more thermolabile groups in the structure than that of ZIF-67 [25]. Fig. 1e shows N₂ adsorption–desorption isotherms of the two catalysts....

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