Materials Research Express

PAPER

Synthesis and structural analysis of beta cobalt hydroxide (β-CoOH) nanosheets derived from ZIF 67 metal-organic framework

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Abstract

In the present work, a facile synthesis of beta-cobalt hydroxide (β-CoOH) nanosheets from ZIF-67 structure using thermolysis method has been described. The cobalt hydroxide nanosheets grown on carbon cloth would be highly beneficial for wide-ranging applications including catalysis and batteries. The XRD studies show that the crystallite sizes are below 100 nanometers for both the ZIF structure and the derived CoOH. The compositional analysis shows that cobalt contributed more to the weight percentage. FESEM images reveal that cobalt nanosheets were grown on the carbon fiber. Also, the TEM images show that nanosheets morphology has been exhibited on the surface of carbon cloth because of the CoOH coating. Further, the chemical composition and purity of the (β-CoOH) nanosheets on CC were perceived using EDX and XPS analyses.

1. Introduction

Nanosheets have been used widely in many applications such as energy storage devices because of their unusual properties pertaining to their ultrathin nature and two dimensional morphologies [1–4]. 2D nanosheets with different morphologies for gas sensing applications have been derived from Metal Organic Frameworks [5]. Nanosheet arrays which involve metal organic frameworks which exhibit supercapacitave properties and excellent electro-catalytic activity are reported [6, 7]. Metal-organic frameworks are compounds in which metal ions are coordinated to organic compounds or ligands. The features of MOFs are their crystalline nature along with their ultrahigh porosity. The atoms occupy only around ten percent of the space and up to 90% of the framework is free. This free space results in the structures that possess enormous internal surface area and volume [8]. The versatile variability of organic and inorganic components of MOFs along with the features like porosity and large free volume make MOFs as molecules of interest for state of the art applications such as thin film devices, catalysis and clean energy [9–11]. Among them, Zeolitic Imidazolate Frameworks (ZIFs) are a new class of porous metal-organic frameworks. ZIFs are composed of tetrahedrally-coordinated transition metal ions such as Fe, Co, Cu, Zn, are bonded and connected by imidazolate linkers [12]. The bonding in ZIF is a coordination bonding that is weaker than covalent bonding in the zeolites thus leading to a kinetically lesser stable bond. This lesser stability enables the substitution by other ligands [13].

In the recent era, more than 105 ZIF topologies have been reported in the literature [14–16]. ZIFs exhibit enhanced thermal and chemical stability. Because of these features, they are extensively used applications in gas adsorption and catalysis [17]. The porosity of the ZIFs employ them in applications like resistance to thermal changes, and chemical stability. Also, ZIFs are being investigated for clean energy applications such as carbon capture and in other separation applications. They also exhibit rapid electron transfer ability which is applied in design of novel materials. By controlling the pore size and its chemistry through the choice of a functionalized linker, ZIFs can be used selectivity to capture CO2 from gas mixtures [18]. ZIFs are being evaluated for several applications, such as gas adsorption [9], molecular separation [15, 16], and catalysis [19, 20]. Various optical and electrochemical mechanisms pertaining to ZIFs are exploited for sensing applications [18, 21–23].
The structural similarity between one of the ZIF structures, Zeolitic imidazolate framework-8 (ZIF-8) composed of Zn ions and imidazolate ligands, with conventional aluminosilicate zeolites is mentionable. This material exhibits inherent porous property, high loading capacity, and pH-sensitive degradation, as well as exceptional thermal and chemical stability[24]. ZIF-67 is a modification of ZIF-8 framework through Zn substitution with Co [25]. ZIF-67 is a wide bandgap material with ~4.3 eV bandgap energy. The composition of ZIF-67 is Co(mIM)2 with cage structure [46,68][26]. ZIF series materials have been widely exploited for Solid-Phase extraction [27–29]. The hopping probability of charge carriers in the mixture is governed by the constitute having lesser activation energy and thus in sensing the ammonia gas using wide bandgap ZIFs, ammonia has a high affinity toward Zn ions and not toward Co ions [30]. The coordination differences between Zn–N and Co–N results in distinct thermolysis routes of ZIF-8 and ZIF-67 in their synthesis and applications. ZIF-8 is easily deformed during heating while decomposes at a higher temperature due to the saturated Zn–N coordination. ZIF-67, however, does not deform during heating due to the stronger Co–N bonds, but easily reacts with oxygen due to the unsaturated Co–N bonds [31–33]. In the present work, Co(OH)2 nanosheets has been synthesized from the ZIF-67 material through the thermolysis method and characterised for possible applications.

2. Materials and methods

All chemicals were of analytical grade and used as received without further cleansing, ZIF-67 (MOF) purchased from XFNANO chemicals, china, ethanol, and water.

2.1. Synthesis of Co(OH)2 from the ZIF-67

Cobalt hydroxide nanosheets have been successfully synthesized by adopting cost effective thermolysis method [34]. Typically, 500 mg of ZIF 67 was dispersed in 100 ml water/ethanol solution, (the ratio is 1:1) to produce a...
precursor solution. Then pre-cleaned carbon cloth (CC) of surface area $1 \times 1 \text{ cm}^2$ was soaked in this precursor solution for the Co-MOF growth at room temperature. After 12 h, the soaked CC covered with Co-MOF was directly transferred to a new precursor solution for another 12 h for growth. After this process, the resultant material was cleaned with pure water and then dried at $70^\circ \text{C}$ for 12 h to form Co(OH)$_2$ supported on carbon cloth (Co(OH)$_2$/CC). The mass loading is around $\sim 3.2 \text{ mg cm}^{-2}$. The schematic representation of the preparation process and the precursor solution are given in figure 1.

2.2. Characterizations
X-ray diffractometer (XRD, SmartLab 9, Rigaku Co.) was employed to identify the crystal structure. The surface morphology and microstructure of prepared samples were characterized by Field Emission Scanning Electron Microscopy (FESEM, JSM-638OLV) and Transmission Electron Microscopy (TEM, JEOL, JEM-2100F). Energy Dispersive x-ray Spectroscopy (EDS, JSM-638OLV) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific) have been used to identify the elemental composition.

3. Results and discussion
3.1. X-ray diffraction (XRD) analysis
The crystalline phase and purity of the prepared sample was characterized by analysing the XRD patterns using CuK$_{\alpha_1}$ with 2\(^\circ\) range from 5 to 90°. The XRD profiles for the bare ZIF 67 (figure 2(a)) and the cobalt hydroxide
\( \beta \)-Co(OH)\(_2\) derived from ZIF-67 (figure 2(b)) samples are given. The observed x-ray peaks of ZIF-67 were compared with the reported values \[35\] and all the peaks are in good agreement with the standard values.

As shown in figure 2(b), the XRD profile confirms the \( \beta \)-Co(OH)\(_2\) phase of nanosized cobalt hydroxide grown on the carbon fibers of the carbon cloth. The hkl values marked in red colour belong to the peaks corresponding to the Co(OH)\(_2\) phase. The observed peak at 16.1° is exactly matched with the reported ZIF-67 peak value \[35\].

The most dominant peaks at 25.8° and 29.7° can be attributed to the presence of the co-existance of ZIF-67 material along with the synthesized \( \beta \)-Co(OH)\(_2\) /CC. Moreover the peaks at 23°, 43.4° and 48.7° belong to the existing Co(OH)\(_2\) phase and were confirmed by standard JDPDS card no. 45-0031. The broadening of the peaks in figure 2(b) indicates the nanosized feature of Co(OH)\(_2\) \[36\].

The structure for cobalt nanoparticle was assigned as hexagonal with space group P3m1 and their lattice parameters are \( a = 3.191 \) Å and \( c = 4.664 \) Å. The average crystallite sizes of bare ZIF67 material and the cobalt hydroxide (\( \beta \)-Co(OH)\(_2\)) derived from ZIF-67 were calculated using Debye–Scherrer’s formula \[37\], and they are found to be 79 nm and 41 nm respectively.

### 3.2. Scanning electron microscopy studies

FESEM images clearly shows the fiber morphology for the carbon cloth (CC) (figure 3(a)) and nanosheets like features for cobalt hydroxide. Figure 3(a) shows the FESEM image for carbon cloth where we can see bunch of uniform fiber like structures with uniform average diameter of 9.3 \( \mu \)m. From figure 3(b), it is obvious that fine two-dimensional (2D) nanosheets are uniformly grown on the surface of the carbon fibers of CC. To understand the presence of nanosized \( \beta \)-Co(OH)\(_2\), FESEM images were recorded at high resolutions and are given in figures 3(c) and (d).

### 3.3. Transmission electron microscopy studies

Transmission electron microscopic images of ZIF-67 derived nanosheets of \( \beta \)-Co(OH)\(_2\) grown on carbon cloth (CC) are as shown in figure 4, these results are in good agreement with XRD and FESEM analyses. Besides, figures 4(a)–(c) reveal that the (\( \beta \)-CoOH)/CC consists of thin, uniform and vertically grown nanosheets. In order to understand the interplanar separation in grown nanosheets, HRTEM images were recorded and are given in figures 4(d) and (e). It is inferred from them that the interplanar separation is about 0.19 nm.
3.4. Energy dispersive x-ray spectroscopy (EDS)

The elemental compositions of the prepared sample was identified using EDS which is given in figure 5. Impurity is not observed for $\beta$-Co(OH)$_2$. Due to the higher contribution from Zeolite structure and the adherence on CC, the elements share an almost balanced distribution in atomic percentage. However, the inorganic cobalt ion shares most of the weight percentage. Homogeneous distribution of elements in the $\beta$-Co(OH)$_2$/CC nanosheets.
including Co, O, and C (from the CC) is observed. The values of the elements in weight and atomic percentage are given in table 1.

3.5. XPS spectroscopy
From figure 6, the XPS survey scan and core-level spectra reveal the valence state of the chemical composition and purity of $\beta$-Co(OH)$_2$/CC. The core-level spectra of Co2p can be decomposed into two spin–orbit doublets and one shake-up satellite peak (Sat.) In the Co 2p XPS spectrum, as shown in figure 6(b), the peaks at 780.35 eV and 797.43 eV are attributed to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ states respectively. Besides, the broad peak at 786.91 eV may be attributed to the satellite peak for Co 2p$_{3/2}$. Meanwhile, the O1s core-level spectra revealing the purity of $\beta$-Co(OH)$_2$/CC.

4. Conclusion
At first time, cobalt hydroxide ($\beta$-Co(OH)$_2$) has been synthesized successfully using a facile thermolysis method. The x-Ray diffraction patterns of ZIF-67 and the cobalt hydroxide nanosheets derived from ZIF-67 were compared with the standard values and found to be in good agreement. The space group, and the lattice parameters were also determined. From XRD, using Debye–Scherrer’s formula the average crystallite size of bare ZIF67 material and the cobalt hydroxide ($\beta$-Co(OH)$_2$) derived from ZIF-67 were calculated as 79 nm and 41 nm respectively. The surface morphology of the samples were studied using FESEM and TEM. The broadening of peaks observed in the XRD pattern validates the formation of nanosheets. The chemical composition and purity of the sample were determined using EDS and XPS which infers that the maximum weight percentage is being shared by cobalt ion.

| Sl no. | Element | Weight % | Atomic % |
|--------|---------|----------|----------|
| 1      | C       | 17.41    | 37.00    |
| 2      | O       | 19.59    | 35.71    |
| 3      | Co      | 63.00    | 27.29    |

Table 1. Elements present in the $\beta$-Co(OH)$_2$/CC sample by EDS.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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