Modification of ZIF-8 using direct mixing method at a room temperature

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Abstract. ZIF-8 modified with CNT doping have been successfully synthesized using direct mixing methods at room temperature. The characteristics of ZIF-8 and ZIF-8 with CNT were studied using XRD and SEM. The structural integrity and phase purity of both materials were obtained through X-ray diffraction patterns and was found comparable to that of sodalite-type ZIF-8. The peaks were found at $2\theta = 7.4^\circ$, $16.5^\circ$, $22.1^\circ$, $25.7^\circ$, $26.7^\circ$, and $32.53^\circ$. When ZIF-8 was doped with CNT, the peaks of ZIF-8 decreased. Scanning electron microscopy of pure ZIF-8 showed hexagonal nanocrystals, and the particle sizes were distributed at approximately 50-140 nm. CNT-doped ZIF-8 showed that ZIF-8 attached to CNT was uniformly with diameters of approximately 80-120 nm. It was concluded that ZIF-8 modified using CNT had been successfully synthesized.

1. Introduction
Zeolitic imidazolate frameworks (ZIFs) are a sub-family of porous metal-organic frameworks (MOFs) built of tetrahedrally coordinated metal ions bridged by imidazolates [1]. The crystal structure of zeolitic imidazolate frameworks (ZIFs) has the same topologies as aluminosilicate zeolites. In zeolites, the framework is built by tetrahedral silicon or alumunium bridged by oxygen atoms. Whereas in ZIF-8, the tetrahedral frameworks are built by transition metal (Zn) as nodes and imidazolate linkers as bridges [2, 3]. Similar to zeolites, the frameworks of ZIF-8 has pores and channels that allow access of guest molecules and can differentiate species on the molecular level. ZIF-8 have more flexibility in surface and structure modification, rigidity, and better thermal, hydrothermal, and chemical stabilities. In 2017, Zhang has successfully modified ZIF-8 structure with rod-like structures [4]. That is advantages ZIFs then zeolites.

ZIF-8 can be synthesized using several methods such as hydrothermal, solvothermal, microwave assisted, and direct mixing. Among those methods, the easiest way to get ZIF-8 is using direct mixing methods. Because it can be prepared in room temperature. Surface area ZIF using this method is 1073 m²g⁻¹ [3].

ZIFs have many advantages on the morphology and properties. It has a uniform porosity and an exceptional chemical and thermal stability. Its made ZIFs have a wide range of promising applications such as supercapacitor using ZIF-67 [5], gas storage [6], drug delivery [7], and chemical sensors [8].
To enhance the ZIFs capabilities several treatment have been done by several treatments such as modified structure, solvent, and modification by another materials. This work reports the use of CNT on ZIF-8 and the influence CNT as modification material on ZIF-8 also investigated on this study.

2. Experimental method
First, 132 mg of Zinc nitrate hexahydrate was dissolved in 12 ml methanol. Second, H-MIM (imidazolate) 1320 mg was dissolved in 60 ml methanol. Then, the two precursor were mixed together drop by drop and stirred for about 30 minutes. The mixtures were washed three times using DI water and methanol. Then, the precipitate was dried at 80 °C for two hours to obtain ZIF-8 powders.

The CNT doping was performed by mixing modified CNT on Zinc nitrate hexahydrate using methanol as solvent. A total of 30 mg CNT and 120 mg PVP were dissolved in 60 ml methanol and stirred 30 minutes and sonicated 1 hour, then centrifuged. The precipitate of CNT was dispersed in 15 ml of methanol. 132 mg of zinc nitrate hexahydrate dissolved on 12 ml methanol. Then dispersed CNT and Zinc nitrate hexahydrate mixed drop by drop and then mixed with H-Mim 1320 mg that dissolved in 60 ml methanol drop by drop under stirred condition afterwards stirred about 30 minutes then centrifuged and washed 3 times using DI Water. Then dried 80°C to get ZIF-8 doped CNT powders. The crystallinity and morphology of ZIF-8 and ZIF-8 doped CNT were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM), respectively.

3. Results and discussion
The diffraction patterns of ZIF-8 and ZIF-8 doped CNT are shown in Figure 1. The XRD pattern of ZIF-8 (in Figure 1) is identical to the presented patterns [1, 9, 10] confirming the successful synthesized. The peaks was found at \(2\theta = 7.4, 16.5, 22.1, 25.7, 26.7, 32.53\). We found the peak of ZIF-8 doped CNT still formed. That indicate the doping of CNT did not disorganize or destroy the assembly of metal (Zn) as nodes and ligands (H-methylimidazole) as frameworks to form ZIF-8 and we also found decreasing the peak of ZIF-8 when doping with CNT (b in Figure 1) and lower than pure ZIF-8. It because when ZIF-8 doped with CNT decreasing concentration of MOF (ZIF-8). As can be seen, The peak of CNT were not appeared. It can be attributed to the high dispersion of CNT in ZIF-8.

Figure 1. XRD pattern of a) ZIF-8, b) ZIF-8 doped CNT.

Figure 2 (a and b) shows the morphology and size using scanning electron microscopy (SEM) of ZIF-8 and ZIF-8 doped CNT. From Figure 2, it can be seen that the morphology of ZIF-8 has diameter of around 50-140 nm while for ZIF-8 doped CNT it is about 80-120 nm. The presence of CNT made
ZIF-8 attached on it. It can be seen on Figure 2 (b) and also made diameter size of ZIF-8 more uniformly. It confirmed the XRD pattern of ZIF-8 doped CNT lower than pure ZIF-8 because the CNT has high dispersed with ZIF-8.

![Figure 2. Morphology images of a) ZIF-8, b) ZIF-8 modified CNT.](image)

4. Conclusion
The modification of ZIF-8 using CNT has been successfully synthesized. The hexagonal morphology of ZIF-8 attached on CNT and made diameter size of ZIF-8 more uniform. The high dispersion of CNT decreases the peaks of XRD patterns of pure ZIF-8.

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