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Surfactant-Assisted Synthesis of Zn(suc)(ina)$_2$ Metal-Organic Framework and Detection of Nitroaromatic Explosives†

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Some traditional techniques, such as hydrothermal synthesis, microemulsion techniques and solvothermal synthesis, are applied to prepare metal-organic frameworks and non-metal-organic frameworks. In this article, we present a morphology-controlled synthesis of non-metal-organic frameworks by using a surfactant-assisted method for potential fluorescent sensing of nitroaromatic explosives. Nanocrystals of three-dimensional (3-D) metal-organic frameworks, Zn(suc)(ina)$_2$. The structures was confirmed by transmission electron microscopy. TEM images of Zn(suc)(ina)$_2$ reveal that size and shape of nanocrystals can be tuned by varying the reaction time. Fluoresent sensing of nitrobenzene to nanocrystal has been studied. The results indicate that nanocrystals of metal-organic frameworks Zn(suc)(ina)$_2$ is highly sensitive to nitroaromatic compounds. The results may be helpful for designing novel fluorescence sensor for the sensing of explosives.

Key Words: Metal-organic frameworks, Nanocrystals, Nitroaromatic compounds, Fluorescence sensing, Explosive detection.

INTRODUCTION

It is known that nitroorganic compounds are molecules with a significant potential for industrial use, particularly as explosives or propellant. Due to the critical antiterrorism situation worldwide and the increased use of explosive materials in terrorism, the development of a detection method for trace explosive materials is highly desirable and necessary in the field of security screening nowadays[1,2]. Although the trained dogs and physical methods such as gas chromatography coupled with mass spectrometer, electron capture detection as well as ion mobility spectrometry are highly sensitive and selective. Some of these techniques are expensive and others are not easily applied to on-site field testing[3]. As method, fluorescence-quenching is proven to be one of the most sensitive and convenient methods for the rapid detection of ultra-trace analytes explosives. The mechanism of fluorescence quenching for explosive detection is attributed to the photoinduced electron transfer from the sensing material to the analyte. This method offers a simple, exquisitely sensitive and rapid detection of explosives in the vapour phase and is now an established technology.

In recent years, much interest has been focused on the design and synthesis of metal-organic frameworks (MOFs)[4], for their interesting structure motifs and potential applications in gas storage, catalysis and molecular sensing[5,6]. More recently, alongside the fast development of nanoscience, increased effort was put into synthesis of the controlled nano- and micro-scaled metal-organic frameworks[7] due to this novel type of nano- and micro-scaled material has potential in a variety of imaging, biosensing, biolabeling and drug delivery applications. Some traditional techniques, such as reverse microemulsion[8], microwave[9] and ultrasound-assisted synthesis[8] are commonly applied to prepare these non-metal-organic frameworks. Herein, we not only present a surfactant-assisted reaction of a nanocrystals of Zn(suc)(ina)$_2$ [**1**, (suc=succinate, ina=isonicotinate)], but also report a highly sensitive to nitrobenzene. The results reveal that nanocrystals of metal-organic framework **1** shows high sensitivity for the sensing of nitroorganic compounds, it may be helpful for designing novel fluorescence sensor for potential detection of explosives.

EXPERIMENTAL

Nanocrystalline powders of metal-organic frameworks were prepared from a stoichiometric amounts of mixture of $Zn(NO_3)_2 \cdot 6H_2O$, isonicotinic acid, succinic acid and CTAB in an aqueous solution of NaOH, the mixture was placed in a 25 mL Teflon-lined autoclave and heated at 160 ºC for a desired reaction time (1, 3, 5, or 8 h)[10]. The nanocrystals were separated by filtration and washed with deionized water (5 m L × 5) and

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absolute alcohol (5 mL × 5) and then dried in air. The yields of the reactions are close to 100 %.

RESULTS AND DISCUSSION

The morphologies and size or nanostructure of the as-prepared samples for different reaction times were characterized by TEM (Fig. 1). As can be seen from the TEM picture, increaseing the reaction time led to the growth of nanocrystals. This result suggests that the reaction time and the presence of CTAB are crucial to the final morphology and size. Hence, it is reasonable to speculate that the cationic surfactant CTAB plays important role in controlling the size and morphology of metal-organic framework, Zn(suc)(ina)$_2$.

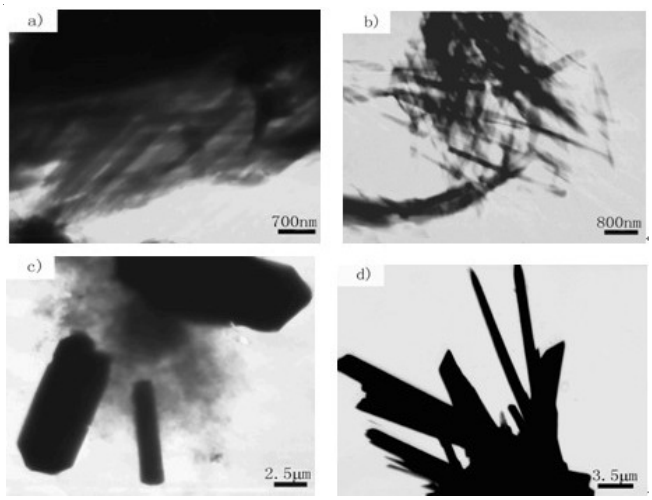

Fig. 1. TEM images of 1 in the presence of CTAB for various reaction times: (a) 1, (b) 3, (c) 5, (d) 8 h

To demonstrate the ability of **1** for detection of explosives, the sensing of nitrobenzene in an acetonitrile solution was quantitatively analyzed by a fluorescence spectrometric titration experiment. Interestingly, the luminescence intensity of the as-prepared nanocrystals is remarkable decreased when the volume of nitrobenzene added. It is known that nitrobenzene is molecules with a significant potential for industrial use, particularly as explosives or propellant. Due to the critical antiterrorism situation worldwide and the increased use of explosive materials in terrorism, the development of a detection method for trace explosive materials is highly desirable and necessary in the field of security screening nowadays, therefore the as-prepared **1** could serve as an ideal candidate for applications in explosives sensing. Corresponding fluorescence spectra of **1** was recorded by injecting different amounts of nitroorganic compounds into a 1 cm cuvette containing 2.00 mL of acetonitrile, in which a slice of glass coated with nanorods of **1** was fixed. And the result of emission intensity with concentration of nitroorganic compounds was shown in Fig. 2. It can be observed that the photoluminescence intensity of **1** increases sharply in response to nitrobenzene. A significantly decrease of emission intensity was observed when 0.2 μL nitrobenzene was added into acetonitrile. Further increase of volume of nitroaromatics solution led to a gradual decrease in fluorescence intensities until 12 μL of stock solution of nitroaromatics were added, at which significant fluorescence quenching effect was observed. All these results suggest that the fluorescence intensity of the as-prepared **1** nanocrystals are highly sensitive to nitrobenzene. Such luminescence properties of **1** nanocrystals are of interest for the sensing of the nitroaromatic and the materials may serve as an ideal candidate for applications in nitroaromatic explosives detection, because many explosive materials, such as the infamous TNT (trinitrotoluene), are based on nitroaromatic compounds.

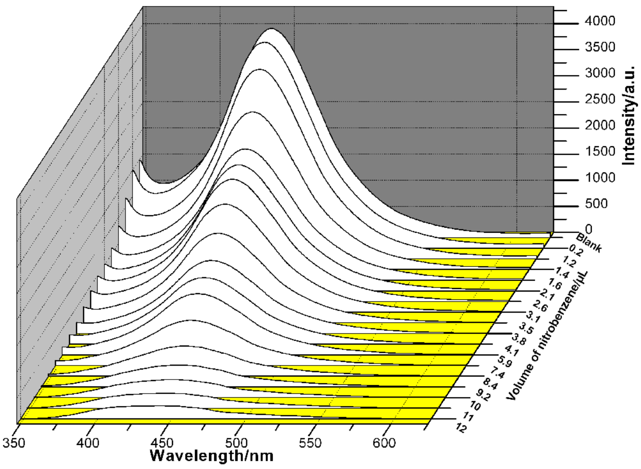

Fig. 2. Variation of emission spectra of **1** nanocrystals with the volume of 9.76 × 10^{-2} M of nitrobenzene in 2 mL of acetonitrile

Conclusion

In summary, we describe a surfactant-assisted method for the synthesis of nanoscale metal-organic framework and fluorescent sensing of nitroaromatic compounds. It was found that the surfactant plays an important role in controlling the sizes and shapes of metal-organic framework nanocrystals and such the surfactant-assisted methodology can be widely applied to synthesize other non-metal-organic frameworks. The fluorescence properties of these metal-organic framework nanocrystals were found to be highly sensitive to nitroaromatic compounds. The result is helpful for the designing of low cost and highly sensitive sensors for nitroaromatic explosives, due to the fact that these materials are inexpensive and the morphology-controlled preparation of metal-organic frameworks nanocrystals can be easily realized as described in this work.

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