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Synthesis and characterization of azine-functionalized zinc cation metal–organic frameworks nanostructures upon silk fibers under ultrasound irradiation, study of pores effect on morphine adsorption affinity

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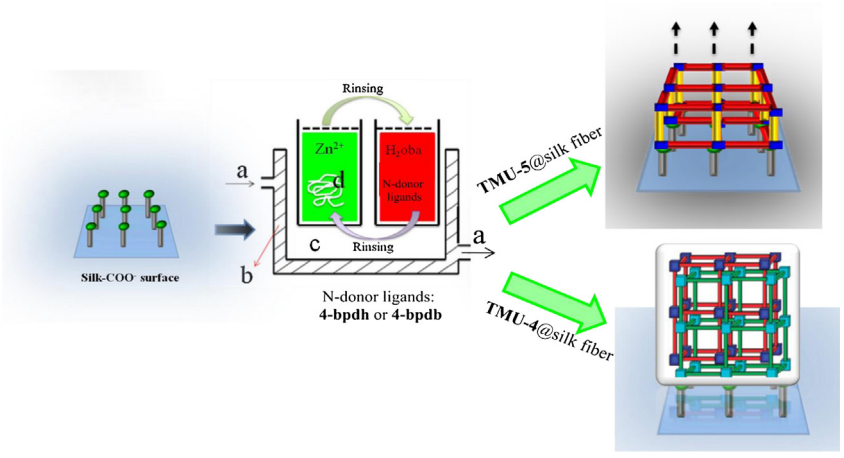
HIGHLIGHTS

- We here present a textile for the removal and extraction of morphine from aqueous samples using Zn(II)-MOFs and silk fibers.
- The effects of sequential dipping steps in growth of Zn(II)-MOFs upon fibers were studied.
- XRPD analyses indicated that the prepared Zn(II)-MOFs upon fibers were crystalline.

GRAPHICAL ABSTRACT



The formation mechanisms of **TMU-4** and **TMU-5** metal–organic frameworks upon silk fiber under ultrasound irradiation.

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ABSTRACT

Thin films of a three-dimensional porous Zn(II)-MOFs (TMU-4 and TMU-5) were deposited on surfaces of silk fiber via a stepwise manner under ultrasound irradiation. The Zn(II)-MOFs@fibers were studied for removal and extraction of morphine from aqueous samples and the effect of host-guest interaction on

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adsorption and desorption efficiency were evaluated. The effect of sequential dipping steps in growth of Zn(II)-MOFs@fiber has been studied. These systems depicted a decrease in the size accompanying a decrease in the sequential dipping steps.

1. Introduction

The field of metal-organic frameworks (MOFs), which are also called porous coordination polymers (PCPs), has been growing tremendously over the last two decades [1,2]. This fascinating class of crystalline hybrid materials, which are formed by association of metal centers or clusters linked by organic ligands, offer an unique chemical versatility combined with a designable framework and an unprecedentedly large and permanent porosity [3–5]. These materials have enormous potential for many practical structure-related applications. This includes the more traditional areas of storage, separation or controlled release of gases, catalysis, sensing, and drug delivery, as well as the adsorptive removal of hazardous materials, which are based on the pore size and shape as well as the host–guest interactions involved [6–11]. However, the majority of these applications are based on the ability of MOFs to behave as hosts for certain molecules. MOFs have already been tested as micro/nanoporous materials with exceptionally high porosity, uniform but tunable pore size, and with well-defined molecular adsorption sites [12]. Apart from their use as bulk materials; these frameworks could be processed as supported homogeneous porous thin films on various surfaces. Controlling the assembly of metal-organic frameworks thin films on different substrates is currently recognized as one of the most important issues in the synthesis of functional materials [12,13]. Different strategies have been developed in the literature to fabricate thin films of MOFs. These technical approaches can be grouped in several ways such as surface functionalization [14], layer-by-layer (LBL) [15] and electrospun nanofibrous filters [16].

In this work we report the layer-by-layer deposition of a microporous Zn(II)-MOF material on the surface of natural silk fiber with −COOH surface functionalization under sonication. The advantage of ultrasonic method is the homogeneous coating of small structures [17]. The Zn(II)-MOFs **TMU-4**@silk fiber and **TMU-5**@silk fiber (**TMU-4** = $[Zn_2(oba)_2(4\text{-bpdb})]\cdot 3DMF$ and **TMU-5** = $[Zn_2(oba)_2(4\text{-bpdh})]\cdot 3DMF$) have been investigated for applications in loading and release of morphine molecules. **TMU-4** shows 1D, large pores with apertures of about 5.3×9 Å, respectively, whereas **TMU-5** shows 3D, interconnected, narrow pores with an aperture of about 4.4×6.2 Å [18]. Morphine is an analgesic opioid and is one of the most potent pain relievers. It has been used for pain relief and other indications for years. Morphine is highly addictive and its use is associated with significant physical and psychological dependence. Morphine has a high potential for addiction; tolerance and psychological dependence develop rapidly, although physiological dependence may take several months to develop.

The deposition of MOF thin films on flexible polymer surfaces might be a new path for the fabrication of functional materials for different applications, such as protection layers for working clothes, gas separation and thin-film drug delivery materials in the textile industry [14]. In anchoring MOFs to surfaces (SURMOFs), the first step is the functionalization of substrate or self-assembled monolayers (SAMs) [19] and the second step is the growth of MOF. Deposition of microcrystalline MOF at alumina [20,21], silica [20] and on surfaces of flexible organic polymers [22] were reported, but in this work we used silk fibers as substrate, thus due to existence of —COOH groups on the surface of these silk fibers no SAM formation was required and in a very simple and effective procedure at ambient pressure and temperature, Zn(II)-MOF coating of the silk fibers were done successfully by LBL technique.

2. Experimental

2.1. Materials and physical techniques

All reagents and solvents were used as supplied by Merck Chemical Company and used without further purification. The silk fiber was obtained from Guilan Silk Company. The natural silk fibers were pre washed using an aqueous solution containing NaOH (pH 9), at 25 °C for 5 min, followed by washed several times with water and dried at ambient temperature. X-ray powder diffraction (XRPD) measurements were done on a Philips X'pert diffractometer with monochromatic Cu Kα radiation. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [23]. The Brunauer–Emmett–Teller (BET) analyses were recorded on Belsorp-mini II japan, and used to determine the specific surface area, pore size and volume. The samples were characterized with a scanning electron microscope (SEM, Philips XL 30 and S-4160) with gold coating. Ultrasonic generators were carried out on a Eurosonic 4D (continuous mode, output power: 350 W). Ultrasonic generators have water circulation system and double jacketed vessel. The effects of sonication in growth of the Zn(II)-MOFs upon fiber were studied in 350 W. The average particle sizes were prepared using Microstructure measurement software. *In situ* UV/vis spectrum experiment has been carried out on a PG Instruments, T80 + UV/vis/NIR spectrophotometer within the wavelength range 190–800 nm, using the same solvent in the examined solution as a blank. Infrared spectra were taken with a FT-IR Bruker, vector 22 spectrometer using KBr pellets in the 400–4000 cm^{-1} range.

2.2. Synthesis of *TMU-4*@silk and *TMU-5*@silk surfaces

The ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) was synthesized according to previously reported methods [24]. Before the experiment began, silk fibers were immersed in an alkaline solution. In alkaline pH, the surface of fiber becomes negatively charged due to deprotonation of the carboxylic group present at the fiber's surface. The growth of **TMU-4**@silk fiber was achieved by sequential dipping in alternating bath of aqueous $Zn(NO_3)_2\cdot 6H_2O$ (0.189 g, 0.64 mmol) and a DMF solution of 4-bpdb (0.238 g, 1 mmol) and 4,4′-oxybisbenzoic acid (H_2oba) (0.254 g, 1 mmol) under ultrasound bath. **TMU-5**@silk were obtained using the same reaction conditions and ratios as used for the isolation of **TMU-4**, but using 4-bpdh (4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) instead of 4-bpdb (Fig. 1). The first layer was fabricated by immersing the silk-COO^- surface into an solution of Zn(II) and then in solution of donor ligands (1 cycle). When negative fiber was immersed in an aqueous solution of zinc(II) nitrate, Zn(II) ions are attracted to the fiber surface. The dipping step in solution of donor ligands allowed the formation of **TMU-4** and initiated the formation of new **TMU-4** particles, as illustrated in Fig. 1.