

A STUDY ON MICROWAVE ASSISTED SYNTHESIS OF METAL ORGANIC FRAMEWORK-199 AND ITS APPLICATION AS AN ELECTRODE MODIFIER

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ABSTRACT

In the present paper, microwave assisted synthesis of metal organic framework-199 (MOF-199) and application as an electrode modifier were demonstrated. The obtained samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS), Scanning electron microscopy (SEM), thermal analysis (TG-DTA) and Fourier transformation infrared (FT-IR). The results showed that MOF-199 with high crystallinity and regular octahedral shape were formed in short time in comparison with solvent-thermal processes. Microwave assisted process is suitable approach to MOF-199 synthesis. The obtained-MOF-199 was used to modifying glass carbon electrodes for determination of uric acid or Pb(II) were addressed.

Keywords: MOF-199, microwave method, Pb(II), uric acid.

INTRODUCTION

MOF-199 ($[\text{Cu}_3(\text{BTC})_2]$ (BTC = 1,3,5-benzenetricarboxylate)) is one of the most important metal organic frameworks (MOFs) due to a large surface area, high pore volume and high chemical stability. Due to these properties, MOF-199 is a potential candidate for gas storage [1], catalysis [2] and sensing applications [3]. In particular, MOF-199 has been employed as an electrode modifier in order to detect glucose [4], to simultaneously determine hydroquinone and catechol [5] and to rapidly detect bisphenol A [6].

Microwaves have been employed for the synthesis of MOFs because the microwave synthesis of MOFs is characterised by the advantages of fast crystallisation [7], phase selectivity [8], diverse morphology/size and rapid heating [9,10], faster kinetics, phase purity, higher yield and reproducibility [11]. In the present paper, we demonstrate the synthesis of MOF-199 using domestic microwave. The use of MOF-199 as an electrode modifier in the differential pulse anodic stripping voltammetric method (henceforth DP-AVS) for the determination of uric acid or Pb(II) has been addressed.

EXPERIMENTAL

Materials

1,3,5-benzenetricarboxylic acid (H_3BTC , 95%) and copper nitrate trihydrate (99%) were supplied by Merck and solvents (dimethylformamide (DMF), ethanol (EtOH) and methanol (MeOH) with 99% purity) were obtained by HiMedia, India. Paracetamol ($\text{C}_8\text{H}_9\text{NO}_2$) and caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) were obtained from Merck, Germany. The phosphate buffer solution was prepared from 1M NaH_2PO_4 and 1M Na_2HPO_4 .

The uric acid (UA) and Pb(II) stock solution, 1000 $\mu\text{g mL}^{-1}$ were prepared by dissolving 0.1000 g of UA or Pb(II) in methanol and diluting with the same solvent to 100 mL in a calibrated flask.

Apparatus

The powder X-ray diffraction patterns of all samples were recorded by a D8 Advance Bruker using a $\text{Cu K}\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$) monochromator. The morphology was examined using a scanning electron microscope (Hitachi S-4800). Thermogravimetric analyses (TGs) were conducted with the TA instrument model, DTG-60H Shimadzu. The nitrogen adsorption/desorption isotherms were performed after dehydration under vacuum at 393 K for 24 h using Micromeritics-ASAP 2020. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) model with a

relative pressure of 0.05 – 0.2. A CPA-HH5 Computerized Polarography Analyzer (Vietnam) was used for the voltammetry experiments. All measurements were conducted in the cell with three electrodes: a GCE (glassy carbon electrode) with a diameter of 2.8 ± 0.1 mm used for formatting the modified electrode as a working electrode, Ag/AgCl/3M KCl as a reference electrode and a platinum wire as an auxiliary electrode. All measurements were performed under ambient temperature.

Preparation of MOF-199

For the solvothermal process, MOF-199 was synthesised according to a modified procedure by reference [3]. Typically, an exact amount of H₃BTC (0.0021 mol) and Cu(NO₃)₂·3H₂O (0.0032 mol) was dissolved in 21 mL of a mixture of ethanol: distilled water: DMF (1: 1: 1 in v/v) in each case and stirred magnetically for 5 minutes. The resulting mixture is loaded into a 250 mL Erlenmeyer flask and placed in hand-made microwave equipment (made from domestic microwave oven - Sharp R-203VN-M with a power capacity of 250 W).

The solid was collected by centrifugation and washed with DMF three consecutive times and dried at 180°C for 8 hours. The samples synthesised by this process were generally named MW-MOF-199.

The electrochemical studies were conducted under ambient temperature. Prior to modification, the GCE was polished with 0.3 and 0.05 μm alumina powder, respectively to a mirror like surface followed by sonication for about two minutes in double distilled water and dried at room temperature and immediately used for modification purposes.

MOF-199 materials were first mixed in the desired solvent (1.0 mg / mL) then placed in an ultrasonic bath for 1 hour. Subsequently, the desired volume of the MOF-199 suspension was casted onto the GCE. The solvent was evaporated by a dryer. The MOF-199 modified GCE was obtained.

RESULTS AND DISCUSSION

Synthesis of MOF-199

The phase structure of the obtained samples was studied by means of XRD measurements. The diffraction peaks of the obtained samples were consistent with the theoretical patterns

from the single crystal data, and with those previously reported of MOF-199 [12] as shown in Figure 1. The sharp peak and high intensity indicate that all the MOF-199 obtained possessed high crystallinity. The intensity of the characteristic diffraction increased sharply for 30 minutes and then decreased slightly

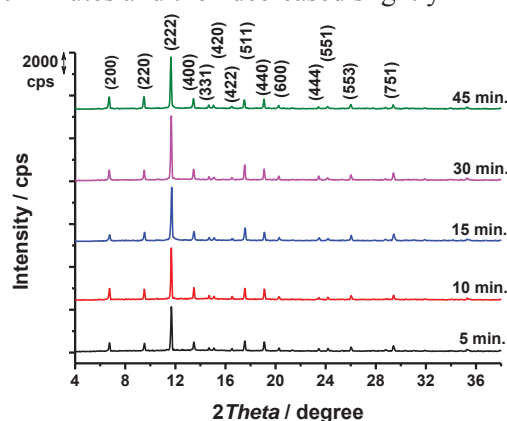


Figure 1. XRD pattern of MOF-199 with different microwave irradiation.

The SEM images of MOF-199 at various reaction times show that the dimensions of the crystals formed increased by an average of 11.1 μm to 22.3 μm with an increasing irradiation time from 5 to 30 minutes (see Figure 3 a1-a4) and then decreased to around 12.6 μm as the irradiation time lasted up to 45 minutes (Figure 3 a5). The average size of particles counted by 50 particles were 12.1 μm ± 2.0 for 5 min., 19.2 μm ± 2.5 for 10 min., 21.8 μm ± 3.9 for 15 min., 22.5 μm ± 0.9 for 30 min. and then 12.6 μm ± 3.3 for 45 min. of the microwave irradiation. The morphology of MW-MOF-199 consisted of octahedron shaped crystals with smooth facets. The well faceted 10-15 μm crystals of MOF-199 are observed at 30 minutes of microwave irradiation.

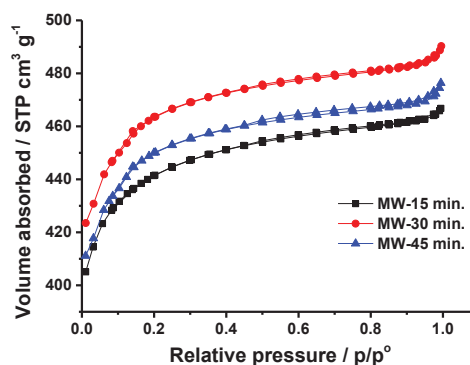


Figure 2. Nitrogen adsorption/desorption isotherms of MOF-199 synthesized at different microwave irradiation times.

The textural properties of MOF-199 were investigated by the nitrogen adsorption/desorption isotherms, as shown in Figure 2. The isotherm curves belong to type I according to the IUPAC classification, which is characteristic for microporous materials. The specific surface areas calculated by the BET model tended to increase as the synthesised time increased and then, slightly decreased for samples with long synthesised times. In fact, the specific surface areas for MOF-199 at 15, 30 and 45 min. of the microwave irradiation were 1554, 1635 and 1562 m² g⁻¹, respectively. It is worth noting that the specific surface area of MOF-199 obtained by the microwave method is significantly higher than those prepared from other methods reported [13,14]. The high surface area of MOF-199 reveals that the microwave synthesis enhances the nucleation and crystal growth steps, reduces agglomeration and produces homogeneous particles with larger surface areas. Moreover, the microwave method requires a short time and provides a high yield compared with the conventional solvothermal method.

The synthesis of MOF-199 by means of the microwave assisted hydrothermal method was reported by Seo et al. [13]. By this method, the reactants were loaded into a Teflon autoclave, sealed and placed in a microwave oven. The autoclave was heated at 140°C – 170°C microwave power. However, these professional microwave devices have a high cost and must be operated in controlled temperatures and pressures. The present study, however, is different from the aforementioned study [13]. An Erlenmeyer flask is equipped with a reflux condenser, therefore the reactions are conducted in mild conditions (ambient atmosphere). The temperature in the Erlenmeyer flask measured through the condenser was around 80 – 100°C depending on the irradiation time.

Electrochemical performance of the MOF-199 based GCE

To expand the applicability of MOF199 as an electrode modifier, in this study we will investigate the potential for electrolyte analysis for Pb (II) and uric acid. The parameters of voltammetric measurements were used according to the literature [15] for Pb (II) analysis and literature [16] for uric acid analysis.

Figure 3 shows the DP-ASV curves of UA oxidation with increasing UA concentration from

1x10⁻⁵ to 5x10⁻⁵ μM. The calibration curves for UA present a good linear response in the concentration range 1.0x10⁻⁵ mol L⁻¹ to 5.0x10⁻⁵ mol L⁻¹. The corresponding calibration equations express as follows:

$$I_{p,UA} (\mu A) = (-0.065 \pm 0.060) + (2.72 \cdot 10^4 \pm 1.80 \cdot 10^3) C_{UA} (M); r = 0.999.$$

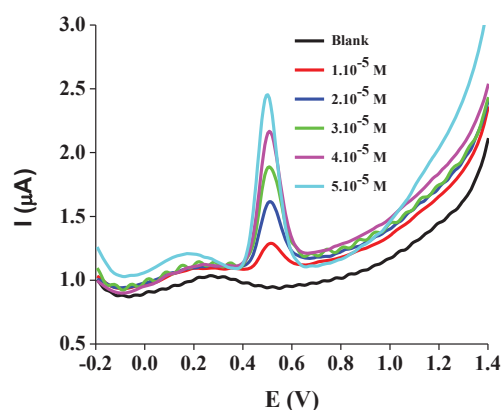


Figure 3. Differential pulse voltammetric curves obtained for the oxidation of UA in a 0.2 mol L⁻¹ acetate buffer solution (pH4.5)

Experimental conditions of DP-ASV: $E_{acc} = -0.2$ V; $t_{acc} = 15$ s; $E_{range} =$ from -0.2 V to 1.4 V; $E_{step} = 6$ mV; $v = 20$ mV s⁻¹; $\Delta E = 60$ mV; $\omega = 1000$ rpm.

The linear regression exhibits very high correlation coefficient ($r = 0.999$). The calculated detection limits is 2.2x10⁻⁶ M.

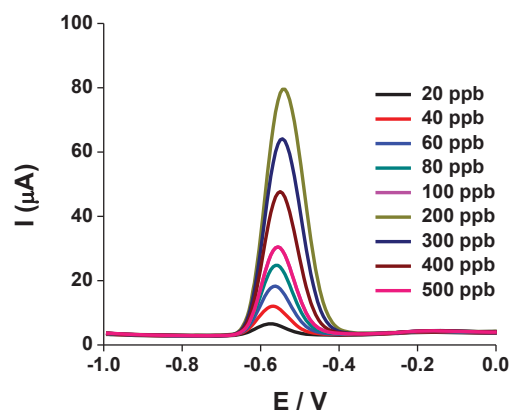


Figure 4. Differential pulse voltammetric curves of Pb(II) in a 0.2 mol L⁻¹ acetate buffer solution (pH4.5) in concentration range of 20 to 100 ppb; 100 to 500 ppb; b) linear plot of I_p and concentration of Pb(II). Experimental conditions of DP-ASV: 0.1 M ABS buffer pH 4.5; $E_{acc} = -1.1$ V; $t_{acc} = 90$ s; $E_{range} =$ from -1.1 V to 0.5 V; $E_{step} = 6$ mV; $v = 20$ mV s⁻¹; $\Delta E = 100$ mV; $\omega = 1000$ rpm.

Experimental conditions of DP-ASV: 0.1 M ABS buffer pH 4.5; $E_{acc} = -1.1$ V; $t_{acc} = 90$ s; E_{range} = from -1.1 V to 0.5 V; $E_{step} = 6$ mV; $v = 20$ mV s^{-1} ; $\Delta E = 100$ mV; $\omega = 1000$ rpm.

The dependence of anodic stripping current (I_p) for Pb(II) on its concentration was conducted by DP-ASV as shown in Figure 4. The I_p of Pb(II) versus its concentration exhibited a nonlinear response in the concentration range of 16–500 ppb. Using the plot of I_p versus added concentrations of Pb(II), two ranges are obtained. The first linear range between 20 ppb and 100 ppb and the second range between 100 ppb and 500 ppb were described by following equations:

Range from 20 ppb to 100 ppb

$$I_p (\mu A) = (-2.904 \pm 1.499) + (0.294 \pm 0.023) \cdot C_{Pb(II)} (\text{ppb}); r = 0.9991;$$

Range from 100 ppb to 500 ppb

$$I_p (\mu A) = (-11.98 \pm 3.705) + (0.154 \pm 0.011) \cdot C_{Pb(II)} (\text{ppb}); r = 0.9992$$

The break in the calibration curve of UA probably reflects the formation of a sub-monolayer in the first range of calibration and formation of a monolayer in the second range. The limit of detection (LOD) calculated in the first range of the Pb(II) concentration was 4.6 ppb. The obtained LOD in this work were compared with the other references [17,18,19]. It could be noticed that the LOD of Pb(II) from the proposed method was lower or comparable with those results based on modified electrodes in previous papers.

The favourable signal-promoting effect of the MOF-199 indicated that it could accelerate the electron transfer rate of UA or Pb(II) and had good electrocatalytic activity for the redox reaction of UA or Pb(II). MOF-199 contains the carboxyl group, aromatic rings, and the transition metal Cu(II). The π - π stacking interaction between the aromatic rings of the UA of MOF-199 were possibly responsible for the accumulation of the UA on the modified electrode. On the other hand, the coordination of the Pb(II) to carboxyl group in MOF-199 also contributed to attracting analytes to the modified electrode surface. The porous structure with a large surface area resulted in a high number of reactive sites that are readily accessible for the target analytes. The combinations of these effects led to a greater amount of UA and Pb(II) accumulation on the surface of MOF-199/GCE, greatly improving the voltammetric signals.

CONCLUSIONS

The synthesis of MOF-199 by means of microwave method has been demonstrated. The microwave method has the advantages of high yield, reduced time and mild conditions (ambient temperature and atmosphere). The obtained MOF-199 possessed higher crystallinity, a morphology characterised by defined octahedron shaped crystals and a large surface area compared to from the results of the solvothermal method. MOF-199 was employed as a GCE modifier and this electrode exhibited an excellent electrocatalytic activity towards the reduction and oxidation of uric acid or Pb(II). The enhanced electrochemistry activity of MOF-199/GCE towards uric acid or Pb(II) were mainly derived from the combined properties of hybrid organic/inorganic MOF-199, such as a strong adsorptive ability and a larger specific area. MOF-199-based GCE promotes the sensitivity of the determination of uric acid with a low detection limit (2.2×10^{-6} M). The peak current of Pb(II) was linearly proportional to its concentration over the range 16 to 100 ppb. The limit of detection and the limit of quantitation were as low as 6.1 ppb. and 12.5 ppb. These results showed that MOF-199 is a potential electrode modifier for both uric acid or lead determination in aqueous solution.

Acknowledgments

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