AMINO-FUNCTIONALIZED METAL-ORGANIC FRAMEWORK-199: SYNTHESIS AND APPLICATION AS AN ELECTRODE MODIFIER

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ABSTRACT

Microwave assisted synthesis of aminoterephthalate functionalized MOF-199 (NH_2-MOF-199) and its application as an electrode modifer were demostrated. 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 microwave assisted process was suitable approach to synthesise MOF-199. The indirect modification of MOF-199 by aminoterephthalate under microwave condition was favorable for to form NH_2-MOF-199. The possible mechanism for grafting aminoterephthalate to MOF-199 surface was proposed. The obtained NH_2-MOF-199 was used to modifying glass carbon electrodes for simulationeous determination of arscorbic and uric acid or Pb(II) and Cd(II) were addressed.
Keywords: MOF-199, microwave, Ascorbic acid, uric acid.

INTRODUCTION

Metal-organic frameworks (MOFs) represent a new class of porous crystalline materials for which it is possible to design organic linkers and inorganic joints. MOFs are crystalline porous coor-dination polymers that can be characterized as infinite 1D, 2D, or 3D networks resulting from the combination of metal species and organic linkers [1]. A well-known MOFs is $Cu_3(BTC)_2$(BTC: benzene-1,3,5-tricarboxylate), which is formed by paddlewheel secondary building units containing Cu(II) dimers coordinatively linked to carboxylic oxygen atoms from organic benzene-1,3,5-tricarboxy-late (BTC) ligands [2]. Due to large porosity and high surface area, $Cu_3(BTC)_2$ offers unprecedented opportunities in heterogeneous catalyst for the aza-Michael reaction [3], toxic gase adsorption [4], antibacterial activity against escherichia coli [5]. Moreover, development of MOFs based composite for the electrochemical field of interest is becoming increasing. For instance, Copper (II)-based MOFs were used as selective electrocatalysts for the reduction of O_2 and CO_2 [6]. Recent reports suggested that Au-SH-SiO_2 nanoparticles supported on MOF was utilized as a sensor for electrocatalytic oxidation and determination of hydrazine and L-cysteine [7] and MOF-199 as effcient electrode modifier for differential pulse anodic stripping voltammetric determination of lead [8].

In this paper, amino-functionalized $Cu_3(BTC)_2$ composite materials were synthesized by several ways. It is used as a novel electrode modifier. The electrochemical sensing performance was evaluated simultalneously Pb(II) and Cd(II), or simultaneously uric acid and ascorsbic acid.

EXPERIMETAL

Copper (II) nitrate trihydrate $(Cu(NO_3)_2.3H_2O)$, 1,3,5-benzenetricarboxylic acid (H_3BTC), *N,N*-dimethylformamide (DMF), 2-amino-1,4-benzenedicarboxylic acid (ABDC), ethanol and chloroform in this work were obtained from Daejung, Korea. Lead and cadimium stock solution were prepared by lead nitrate $(Pb(NO_3)_2)$ and cadimium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$ (Merck, Germany) in 100 mL 1% (v/v) nitric acid, respectively. Uric acid (UA) and arscorbic acid (AA) stock solutions were prepared from uric acid $(C_5H_4N_4O_3)$, arscorbic acid $(C_6H_8O_6)$ (Daijung, Korea).

MOF-199 was synthesised using microwave method. Typically, an exact amount of H_3BTC (0.0021 mol) and $Cu(NO_3)_2.3H_2O$ (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 was 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 $180^{o}C$ for 8 hours.

NH_2-$Cu_3(BTC)_2$ materials were synthesized by two ways based on a previous literature after a minor modification [8]: For the first way (direct method), copper (II) nitrate trihydrate (0.0041 mol), H_3BTC (0.0022 mol), ABDC (0.0008 mol) were dissolved in a beaker containing DMF (7 mL), de-ionized water (7 mL) and ethanol (7 mL) was loaded into a 250 mL Erlenmeyer flask and placed in hand-made microwave equipment for 30 min. After, the solid was washed with DMF and ethanol, and immersed in chloroform, which was decanted and replaced with fresh chloroform two times over three days. The second way (indirect method): 0.5 gram of the obtained MOF-199 was immersed in 10 mL of 0.1 M $Cu(NO_3)_2$ solution for 2 hours and then add 5 mL of ABDC (0.0010 mol ABDC) under ultrasonicate stirring. The NH_2-MOF-199 was collected by the centrifugation and washed with DMF and ethanol, and immersed in chloroform.

Prior to modification, the glassy carbon electrode (GCE) was polished with 0.02 μm alumina powder to a mirror like surface followed by sonication for about two minutes in double distilled water and dried at room temperature. NH_2-MOF-199 material was first dispersed by ultrasonication in an analytical solvent (1.0 mg/mL) for 1 hour to get a suspension. Then, this suspension was mixed with nafion solution (1.25 % in ethanol) in the ratio of 1:4 by volume. After that, 5 μL of the aliquot was cast onto the GCE. The solvent was evaporated by a dryer. After the modification, the electrode was washed with double distilled water and then left to dry in the air before the electrochemical studies were carried out.

DP-ASV voltammograms were recorded from –0.5 V to + 0.9 V at a scan rate of 0.02 $V.s^{-1}$. DP-ASV voltammograms of blank solution (a solution of double-distilled water without PRC) were similarly recorded before each measurement. The technique parameters of voltammeric measurements were carried out according reference [9] for simultaneous determination of Pb(II) and Cd(II) and reference [10] for simultaneous determination of ascorbic acid and uric acid.

RESULTS AND DISCUSSION

Microwave synthesis of MOF-199

Figure 1a shows XRD patterns of MOF-199. As can be seen from the figure characteristic diffractions of (200), (220), (222), (400), (331), (420), (422), (333), (440), (600), (444), (551), (553), (733), (751), (931), (773) for MOF-199 as references [11,12,13] are observed indicating that the MOF-199 with space group $Fm\overline{3}m$ [2] was obtained. The well-defined octahedral crystals of MOF-199 with around 10 μm in sizes are observed by SEM (see Figure 1b).
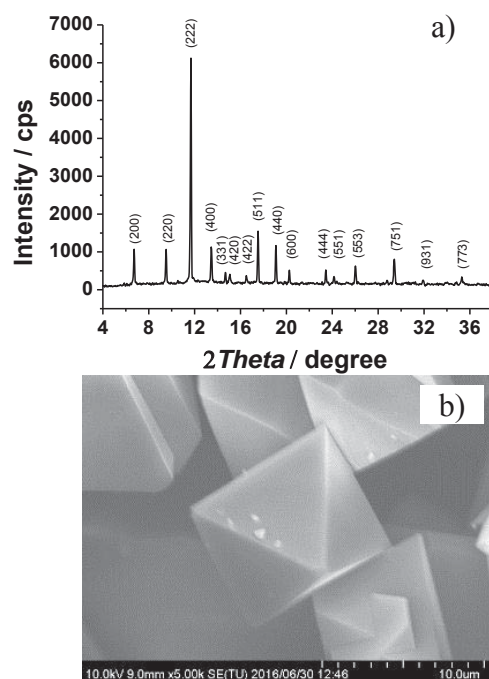

Figure 1. *a) XRD patterns of MOF-199, b) SEM observation of the obtained MOF-199.*
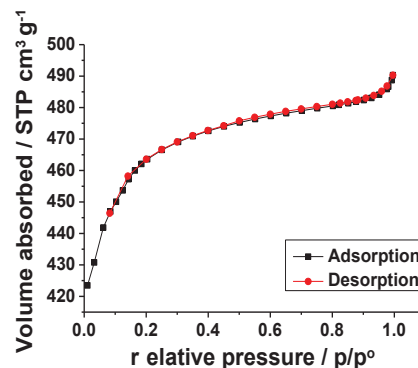

Figure 2. *Nitrogen adsorption/desorption isotherms of MOF-199.*

The textural properties of MOF-199 were studied by nitrogen adsorption/desorption isotherms (see Figure 2).

The isotherm curves belongs to the type I according to IUPAC classification which is characterictic for microporous materials [14]. The specific surface areas calculated by BET and Langmuir model are 1635 m^2/g and 2071 m^2/g, respectively. These value is higher than those of MOF-199 synthesied by conventional solvolthemal method [3,15,16].

Modifying MOF-199 using 2-aminobenzene-1,4-dicarboxylic acid

Figure 3 presents SEM observation of NH_2-MOF-199 synthesized by direct method.
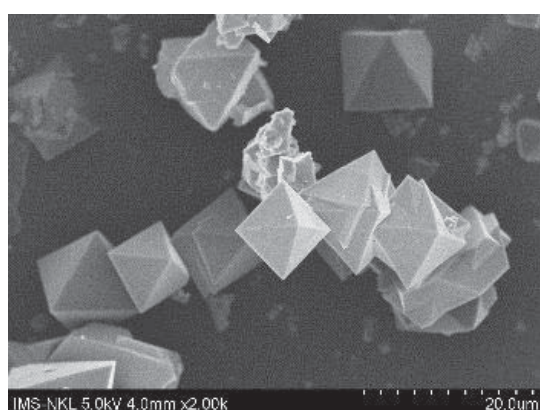
Figure 3. *SEM observation of MOF-199 modified by direct method.*

From the figure, the octahedral crystals of MOF-199 was distributed separately with irregular shape particles as inclusion which may be the compound of ABDC and copper (II).

The modification of MOF-199 was performed by indirect method. Figure 4 presents SEM image of the obtained NH_2-MOF-199.

Figure 4. *SEM image of NH_2-MOF-199.*

In contrast to the smooth face of well cubic shape crystal in Figure 3, the crystal surface

texture of NH_2-MOF-199 was changed dramatically and flocculent substances appeared in the surface. This may be caused by impurities or a second phase nucleating on the surface of the crystals. That is, the Cu–ABDC started to nucleate on the surface of the crystals when the reaction between ABDC and Cu salt to make the Cu–ABDC is performed at a lower temperature.
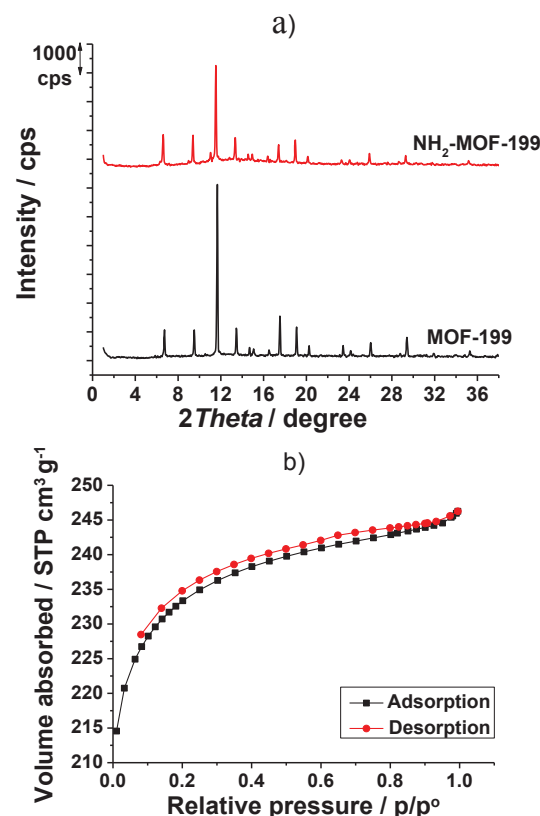
Figure 5. *a) XRD patterns of MOF-199 and NH_2-MOF-199; b) nitrogen desorption/desorption isotherms of NH_2-MOF-199.*

Figure 5 presents the XRD patterns of MOF-199 and NH_2-MOF-199. The positions of diffractions are similar. However, the intensity of diffractions for NH_2-MOF-199 are lower than those of MOF-199 indicating that the original structure of MOF-199 is not altered.

The isotherm curves of NH_2-MOF-199 belongs to type I according to IUPAC classification. The surface area reduction from 1635 m^2 g^{-1} for original MOF-199 to 822 m^2 g^{-1} for NH_2-MOF-199 is due to the occupy of pore in MOF-199 by Cu-ABDC.

The grafting amine group to MOF-9 could be explained as follows: First, the MOF-199 was stirred from a Cu (II) solution to bring Cu(II) to the surface of the MOF-199 and to occupy all empty bonds. The ABDC was then added to bond Cu(II) on the surface of the material

forming the NH$_2$-MOF-199 material. This argument was illustrated in schematic 1.
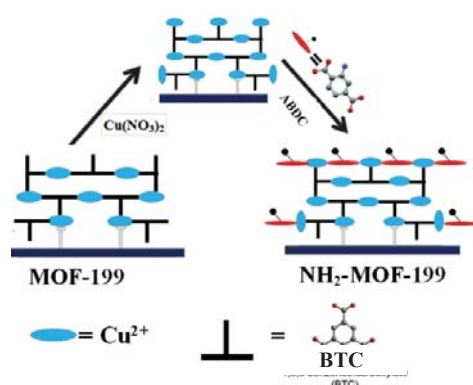
Schematic 1. *Proposed mechanism of the modification of MOF-199 by amine group.*

In this study, we present only some potential applications of NH$_2$-MOF-199 as electrode modifier without going into electrode development to analyze one or more specific substances. The obtained NH$_2$-MOF-199 was used to modify the glass carbon electrode for determine simultaneously Pb(II) and Cd(II) or ascorbic acid and uric acid.

Application of NH$_2$-MOF-199 as an electrode modifier

Simultaneous determination of Pb(II) and Cd(II) was also performed by DP-AVS method. The Cd(II) and Pb(II) were estimated simultaneously increasing their concentrations in a 0.1 M acetate buffer solution (ABS), pH 4.5.

Figure 6a presents the DPV-AVS curves obtained for solution containing equal concentration of Cd(II) and Pb(II) in the range of 5 ppm to 30 ppm. The DP-AVS curves presented oxidation peaks at around -0.87 V for Cd(II) and -0.65 V for Pb(II). The peak separation of about 0.28 V clearly allows the simultaneous determination of these ions.

There are linear correlation of I_p and its concentrations. The linear regression was as follows:

For Cd(II): $I_{P,Cd(II)}$ (µA) = (-0.0353 ± 0.00332) + (0.0283 ± 2.70.10^{-4}) $C_{Cd(II)}$ (ppb); R^2 = 0.9995.

For Pb(II): $I_{P,Pb(II)}$ (µA) = (-0.108 ± 0.0131) + (0.0570 ± 0.00110) $C_{Pb(II)}$ (ppb); R^2 = 0.9981.

The limit of detection (LOD) calculated in the range of the Pb(II) and Cd(II) concentration from 5 ppb to 30 ppb was 1.0 ppb and 1.8 ppb.
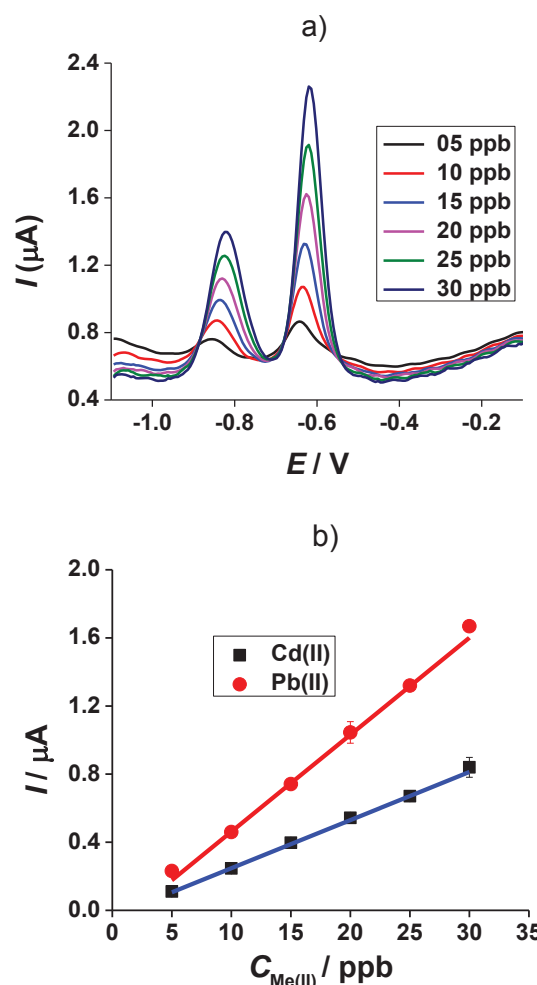
Figure 6. *a) DP-ASV curves of PRC on its concentration in the range of 5 to 30 ppm in 0.1 M ABS buffer pH 4.5; b) the linear regression of I_{ap} versus concentrations (t_{acc} (accumulate time) = 90 s, E_{acc} (accumulate potential) = -1,1 V, scan rate = 0.01 V s^{-1}, ΔE = 0.1 V).*

Simultaneous determination of AA and UA was also performed by DP-AVS method. The AA and UA were determined simultaneously increasing their equal concentrations in a 0.1 M phosphate buffer solution (PBS), pH 7 (Figure 7a). The DP-AVS curves presented oxidation peaks at around +0.18 V for AA and +0.49 V for UA. The peak separation of about 0.31 V clearly allows the simultaneous determination of these compounds.

The dependence of anodic stripping current (I_p) for AA and on its concentration was conducted by DP-ASV as shown in Figure 7b. The I_p of AA *versus* its concentration exhibited a nonlinear response in the concentration range from 30 µM to 548 µM. The first linear range between 30 µM and 119 µM and the second

range between 167 μM and 548 μM were described by following equations:

$I_{P,AA} = (-1.03 \pm 2.22) + (0.299 \pm 0.022).C_{AA}$; $r = 0.9916$ ($n = 4$)

$I_{P,AA} = (20.07 \pm 0.33) + (0.122 \pm 0.001).C_{AA}$; $r = 0.9996$ ($n = 8$)

The limit of detection (LOD) calculated in the range of the AA concentration from 30 ☐M to 119 ☐M was 22.9 ☐M.
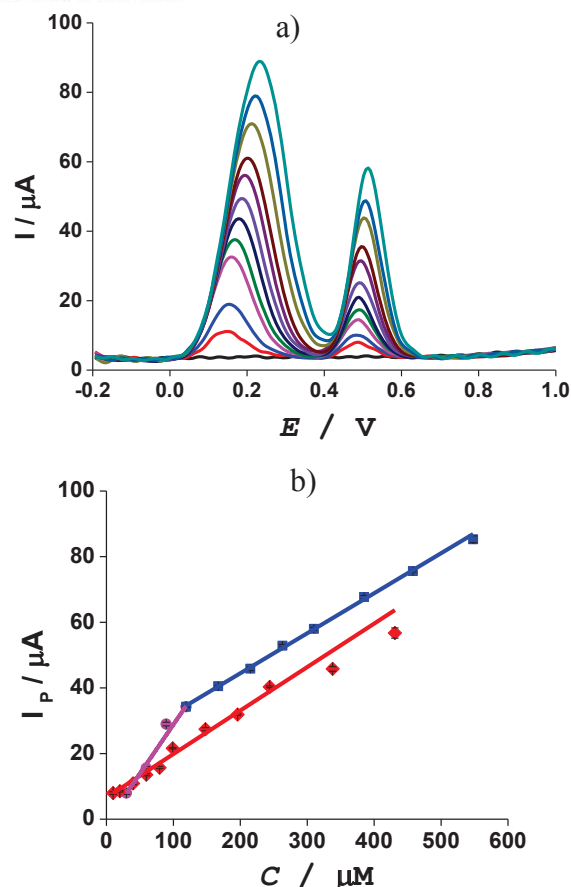
Figure 7. *a) DP-ASV curves of AA and UA on its concentration in the range of 30 to 548 μM and 10 to 431 μM in 0.1 M PBS, pH 7, respectively;   b) the linear regression of I_{ap} versus concentrations ($t_{acc} = 15$ s, $E_{acc} = 0$ V, scan rate = 0.01 V s^{-1}, , $\Delta E = 0.1$ V).*

While the plot of $I_{p,UA}$ *versus* its concentration provided highly linear regression and were expressed by following equation:

$I_{P,UA} = (6.60 \pm 0.85) + (0.133 \pm 0.006).C_{UA}$; $r = 0.9899$ ($n = 11$)

The limit of detection (LOD) calculated in the range of the UA concentration from 10 ☐☐ to 245 μM was 24.6 μM.

It could be noticed that the LOD of AA and UA from the proposed method was slightly lower   those results based on modified electrodes in previous papers [17]. The LOD of Pb(II) and Cd(II) was lower or comparable with those results based on modified electrodes in previous papers [18,19]. This is only a preliminary results. An optimization of technical parameters should be studied to reduce LOD. The results show that the NH$_2$-MOF-199 material has the potential to be an electrode substance to simultaneously identify many organic and inorganic substances in aqueous solution.

CONCLUSION

MOF-199 materials with high crystallinity, octahedral shapes, and about 10 μm in size were successfully synthesized by microwave method. 2-amino-1,4-benzenedicarboxylate indirectly grafted to MOF-199 by ultrasonic assisted method and amine groups adheres to the surface of the material, without altering the structure of the original MOF-199. The results obtained in this work demonstrate the potentiality of the aminoterephthalate functionalized MOF-199 for the simultaneous determination of AA and UA, or Pb(II) and Cd(II) , with LOD of 22.9 μM and 24,6 μM or 1.0 ppb and 1.8 ppb, respectively.

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