Electronic Supplementary Information

Nickel-metal organic framework ultrathin nanobelts based electrochemical sensor for determination of urea in human body fluids

Cancan Bao¹, Qiangqiang Niu¹, Zi-Ang Chen¹, Xiaowei Cao², Hui Wang¹, Wenbo Lu¹.*

¹ Key Laboratory of Magnetic Molecules and Magnetic Information Materials (Ministry of Education), School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, China;
² Institute of Translational Medicine, Medical College, Yangzhou University, Yangzhou 225001, China;

* To whom all correspondence should be addressed:
E-mail: luwb@sxnu.edu.cn (W.L.); Tel.: (+86)357-2051192; Fax: (+86)357-2051192.
Experimental Section

Reagents

Nickel acetate tetrahydrate (Ni(CH$_3$COO)$_2$·4H$_2$O) is purchased from Tianjin Guangfu Fine Chemical Research Institute. Potassium hydroxide (KOH), sodium chloride (NaCl) and sodium sulfate (Na$_2$SO$_4$) are purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Glutaric acid (HOOC(CH$_2$)$_3$COOH), cytosine, thymine, adenine and uric acid are purchased from Aladin Ltd. (Shanghai, China). When the above-mentioned reagents are used for experiments, without any pretreatment. Deionized (DI) water used throughout all experiments. The human urine samples are kindly provided by graduate students of our group in Shanxi Normal University (Linfen, China).

Materials Characterization

Transmission electron microscopy (TEM) measurements are performed on a JEM-2100 (JEOL, Japan) with an accelerating applied potential of 200 kV. The samples for TEM characterization are prepared by placing a drop of the dispersion on carbon-coated copper grid and dried at room temperature. Fourier Transform Infrared spectroscopy (FT-IR) measurements are finished on a FT-IR Spectrometer TENSOR 27 (Bruker Optik GmbH, Ettlingen, Germany). Scanning electron microscopy (SEM) tests are achieved on JSM-7500F SEM (JEOL, Japan) at an accelerating applied potential of 20 kV. The samples for SEM characterization are
conducted by placing a drop of the dispersion on a bare Si substrate and air-dried at ambient temperature. Electrochemical measurements are accomplished with CHI 660E electrochemical analyzer (CH Instruments Ins., Shanghai). A conventional three electrode cell is applied. The glassy carbon electrode (GCE) (geometric area = 0.07 cm$^2$) is taken as the working electrode. The Ag/AgCl (saturable KCl) electrode is served as the reference electrode. And a platinum wire is regarded as the counter electrode. All potentials obtained in this experiment are referred to the Ag/AgCl electrode. All the tests are processed at room temperature.

**Preparation of Ni-MOF ultrathin nanobelts**

Ni-MOF nanobelts are synthesized according to a previous method with a little modification [J. Mater. Chem. B, 2017, 5, 5234-5239]. In a typical synthetic procedure, 0.7920 g of glutaric acid, 0.9880 g of nickel acetate tetrahydrate, and 0.4600 g of potassium hydroxide are dissolved in a mixture solution (40 mL) containing ethanol and deionized water, where the ratio by volume of ethanol and deionized water is 1:1. Under the condition of stirring, a solution with color similar to Ni (II) is obtained when the before-mentioned mixture is dispersed in 0.064 g of NaOH (0.4 M) solution. Next, we divert this solution from beaker to a 100 mL of Teflon-lined autoclave, holding 180 °C for 2 days. Finally, the green precipitate is collected by centrifugation with 9000 rpm for 6 min, with DI water and ethanol to wash precipitate, dried at 80 °C for 12 h.
**Preparation of Ni-MOF sensor**

The glassy carbon electrode (GCE) is polished before modification with 0.3 μm and 0.05 μm alumina slurry on a microcloth polishing pad successively, and sonicated in DI water and ethanol respectively. The electrode is decorated with prepared solution by drip method, that is, the 2 μL of uniform suspension is directly dropped onto the surface of the GCE and dried under infrared light. Then it is fixed with 1% Nafion solution. The Ni-MOF sensor is accomplished and a series of electrochemical tests are performed.

**The real sample analysis**

The human urine samples are kindly provided by graduate students of our group in Shanxi Normal University (Linfen, China). The main purpose and application of this research are informed and agreed by the graduate students. For urine samples, the 0.03% of ascorbic acid is added into 1 mL urine samples, and they are also restored at 4 °C before using.
Fig. S1. The XRD patterns of Ni-MOF nanobelts before and after testing.

Fig. S2 The SEM of Ni-MOF after testing.
**Fig. S3.** Plot of anode peak potential (Epa) vs. logarithm of scan rate.

![Graph showing Epa vs. Log V with a linear regression line and R² = 0.983.]

**Fig. S4.** DPV of the Ni-MOF/nafion/GCE electrode without urea in the potential of 0.55V - 0.85V.

![DPV graph with a peak at 0.7V and a potential range of 0.55V to 0.85V.]

Current /µA

Potential /V

0.0 0.55 0.60 0.65 0.70 0.75 0.80 0.85

16.8 12.6 8.4 4.2 0.0

y = 0.136 x + 0.794
Fig. S5. (A) Amperometric response of Ni-MOF electrode in 0.1 M KOH solution towards addition the concentration of 0.2 mM urea at different working potentials (0.50 ~ 0.65 V). (B) The calibration curves of the Ni-MOF electrode at various potentials.
Fig. S6. Calibration curve showing $I_p$ ($\mu A$) vs. $C$ (mM) linear analysis with urea concentration more than 1.0 mM.

Fig. S7. The histogram for the effect of interferences on the current response.
**Fig. S8.** Long-period stability of the urea sensor for different days (0~30 days).

**Fig. S9.** Reproducibility of five electrodes prepared with the same method in 0.1 M KOH containing 1.0 mM urea solution.