***Supporting Information***

# Supplementary Data

**Experimental section**

***Preparation of Ni-MOF*:** C5H8O4 (HOOC(CH2)3COOH, 0.3959 g), KOH (0.2292 g) and Ni(CH3COO)2.4H2O dissolved in a mixture solution (20 mL) containing 1:1 ethanol and deionized water. The mixture was then dispersed in a NaOH (2 mL, 0.4 M) aqueous solution under stirring. Subsequently, the solution was transferred into a Teflon-lined autocalve (50 mL) under the condition of 180 oC for 48 h, then cooled down to room temperature. Finally, the MOF was washed several times with deionized water and ethanol.

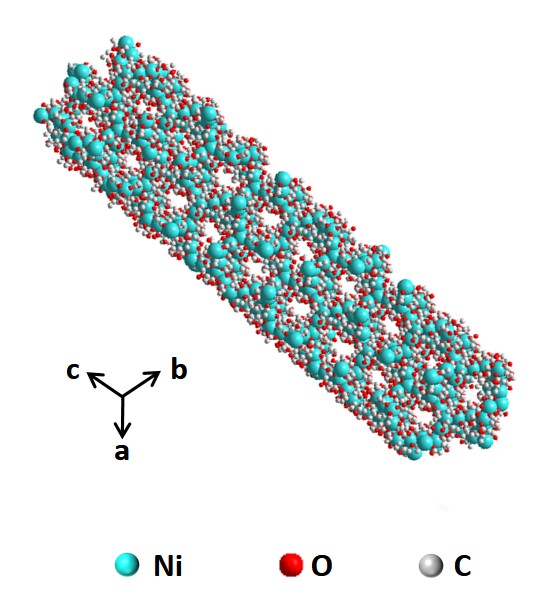
***Preparation of Ni/NiO ultrathin nanobelts***: To obtain Ni/NiO ultrathin nanobelts, the Ni-MIL-77 ultrathin nanobelts were heated in air at 350 oC with a temperature ramping rate of 1 °C min-1.

***Preparation of real samples***: Firstly 12.5 mL borax saturated solution was added under a boiling water bath for 15 min, then 2.5 mL of 30% ZnSO4 solution was used to precipitate protein. After cooled down, the resulting mixture was diluted to 50 mL.

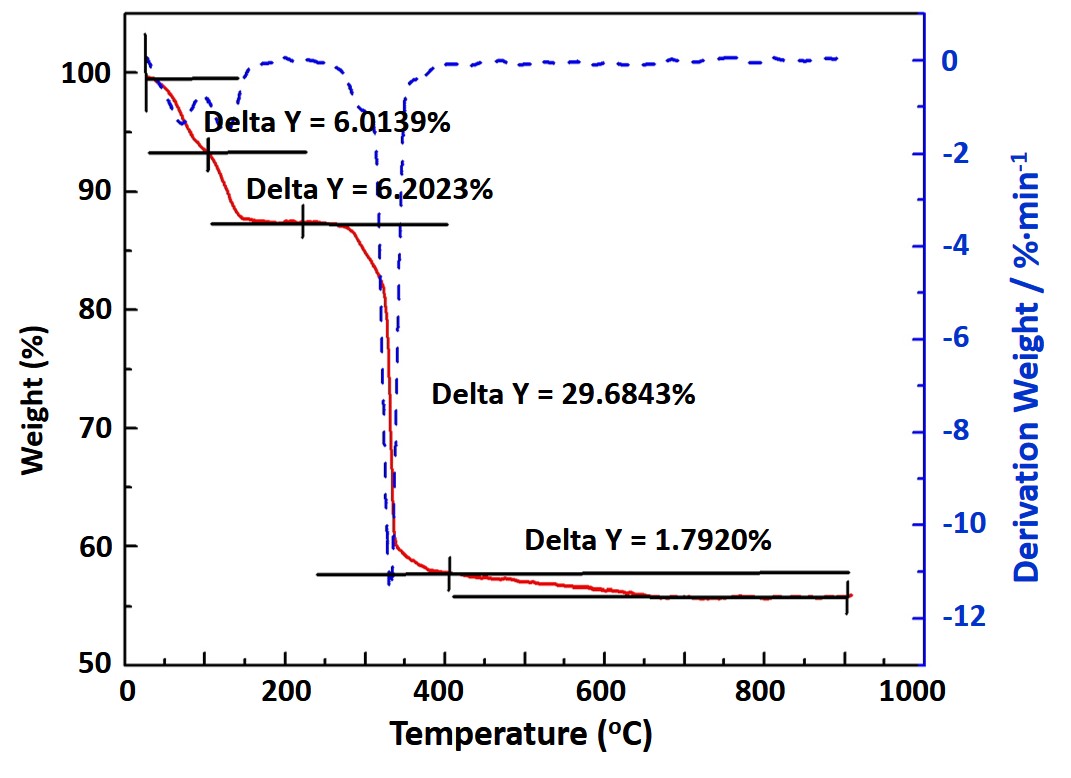
***Laviron’s equation***

Where α is the electron transfer coefficient, n is the number of electron transferred, E0‘ is the formal potential, ʋ is the scan rate. R, T and F have their conventional meanings.

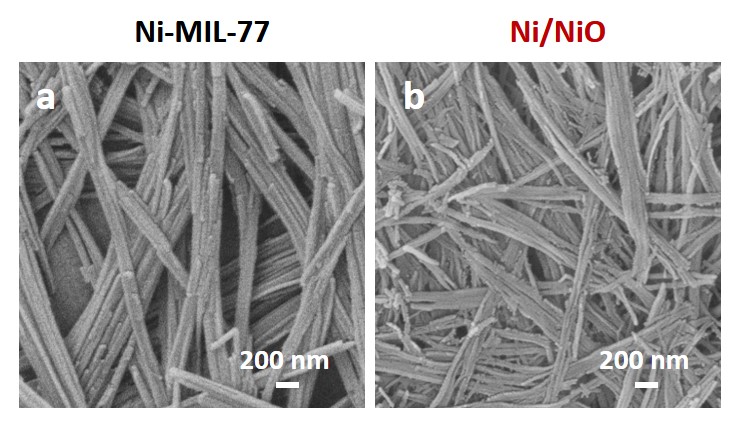
**Section B.** **Supplementary Data**



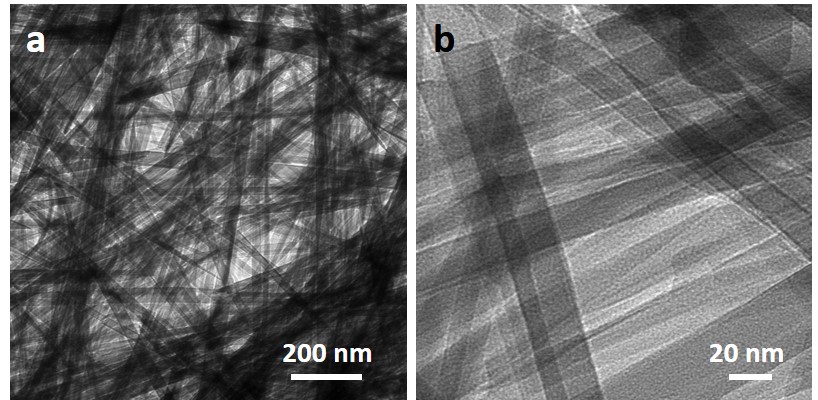
**Figure S1**. Structure diagram of Ni-MIL-77.



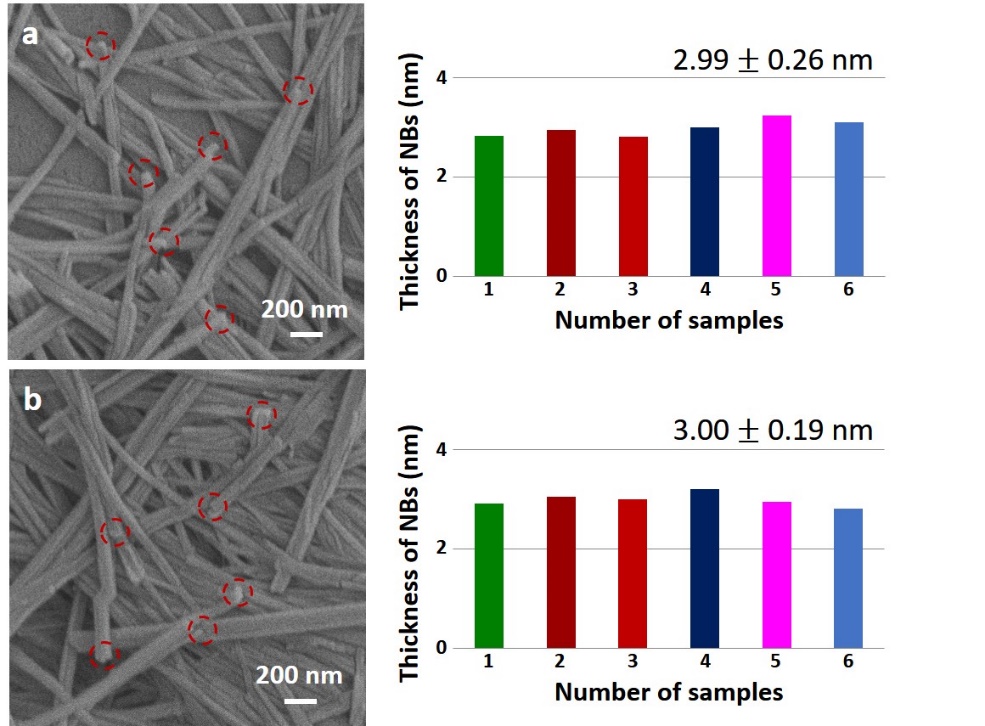
**Figure S2**. Thermogravimetric curve of Ni-MIL-77 in air with a heating rate of 1 °C min-1.



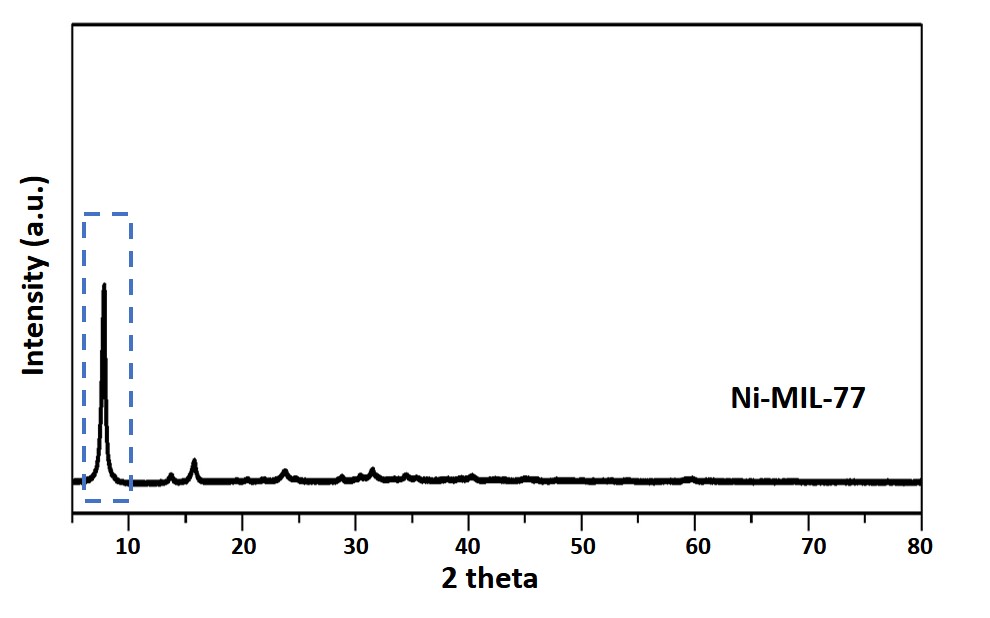
**Figure S3**. SEM images of a) Ni-MOF; b) Ni/NiO.



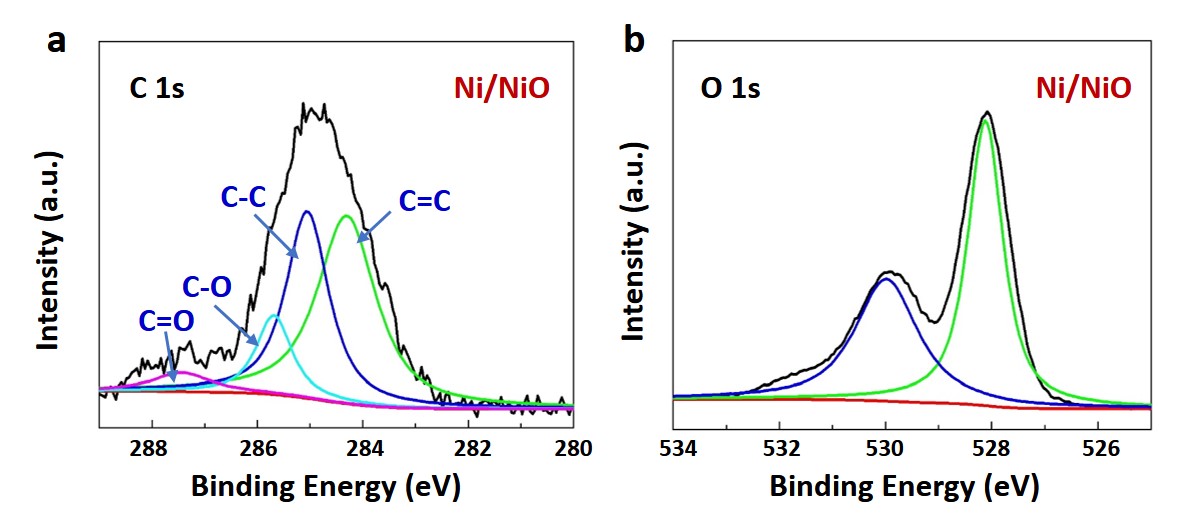
**Figure S4**. TEM images of Ni-MOF.



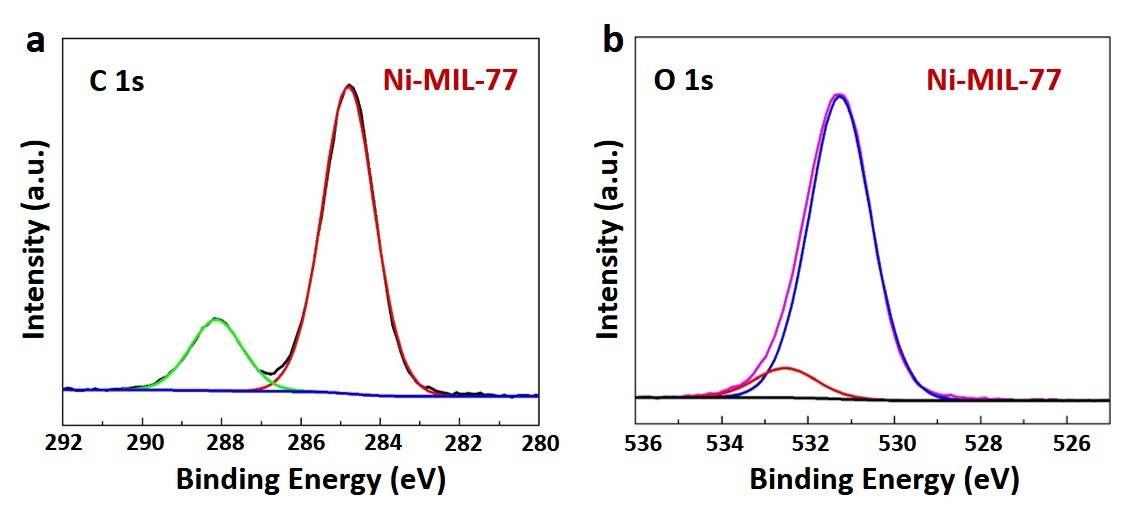
**Figure S5**. Analysis of the thickness of the selected area at random in the SEM images of Ni/NiO nanobelts, the right side is the corresponding size distribution histogram.



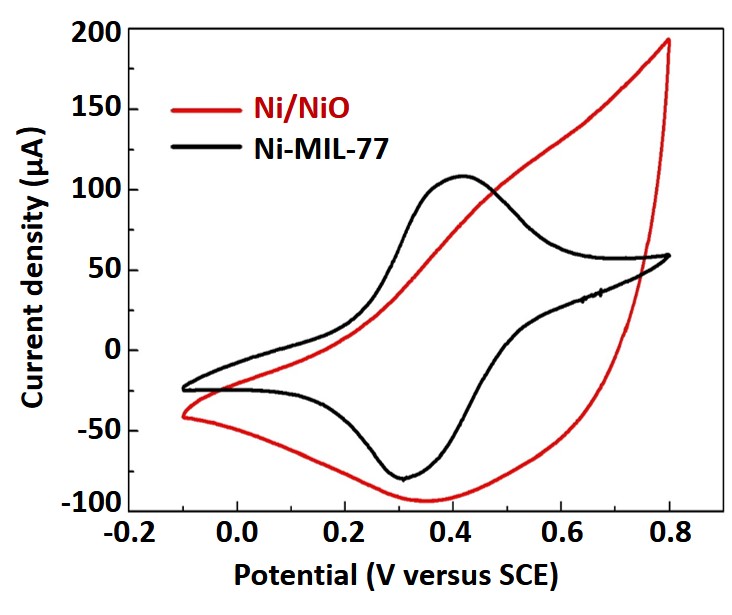
**Figure S6**. XRD patterns of the Ni-MIL-77, strong peak of 5o as the Ni-MIL-77 characteristic peak.(Guillou et al., 2003)



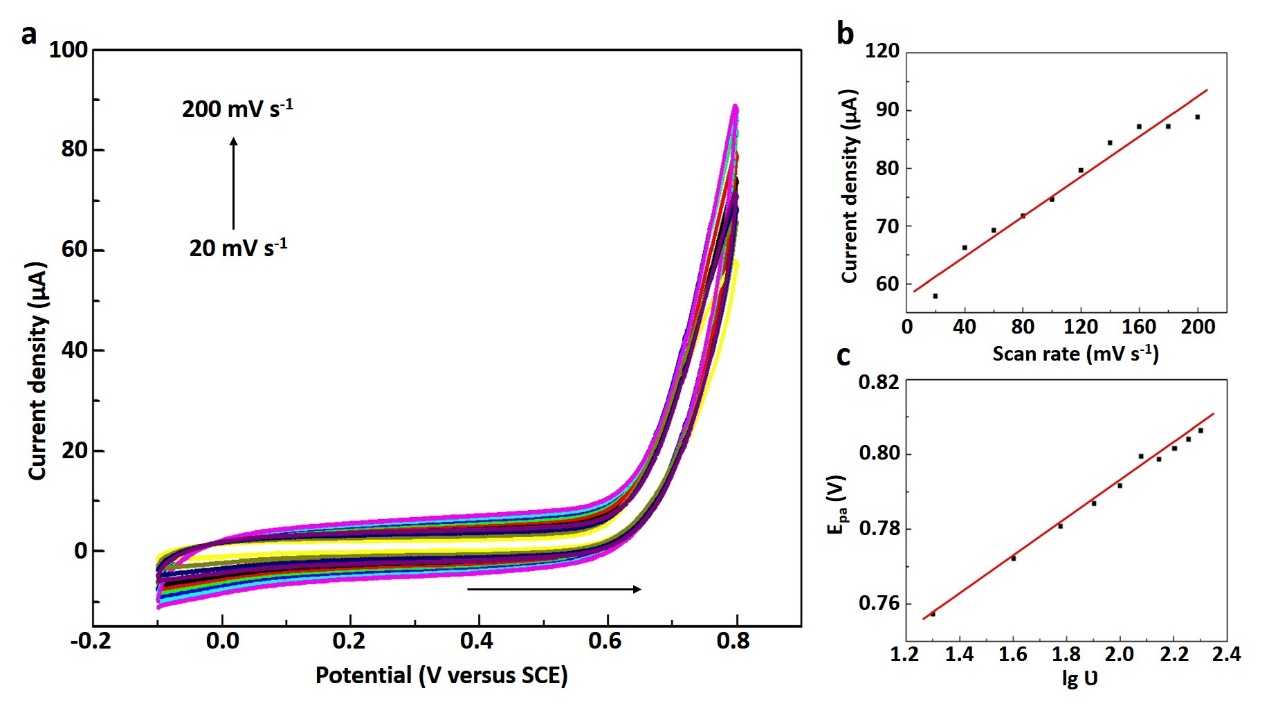
**Figure S7**. a) C 1s and b) O 1s XPS spectra of Ni/NiO.



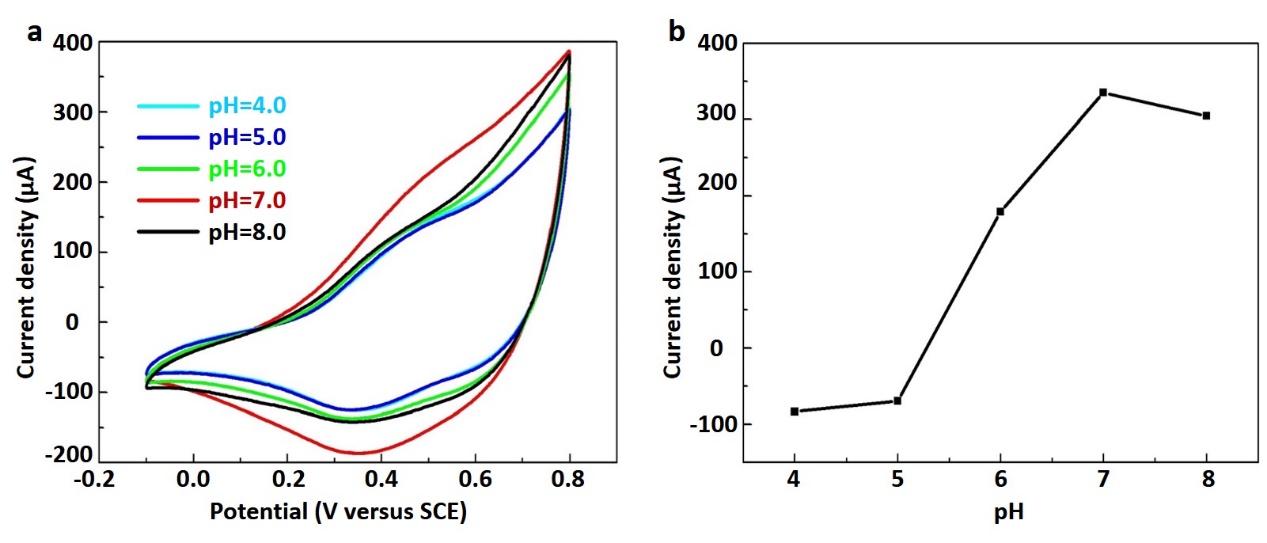
**Figure S8**. a) C 1s and b) O 1s XPS spectra of Ni-MIL-77.



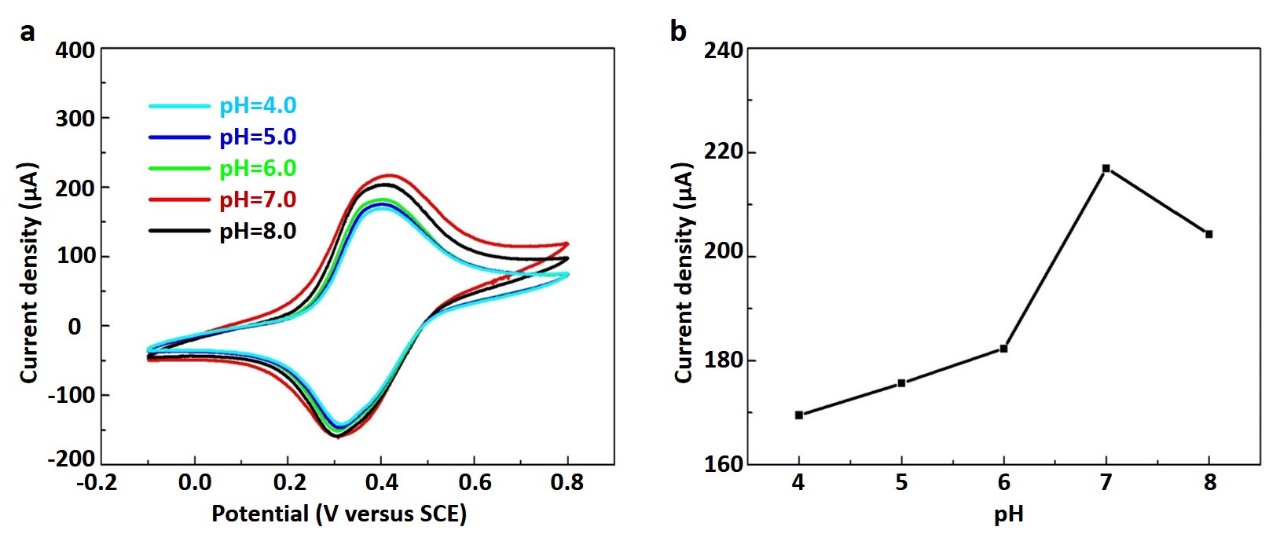
**Figure S9**. At a scan rate of 50 mV s-1 in 5.0 mM K3Fe(CN)6 + 1 M KCl solution, CV curves over a potential range of -0.1-0.8 V (versus SCE).



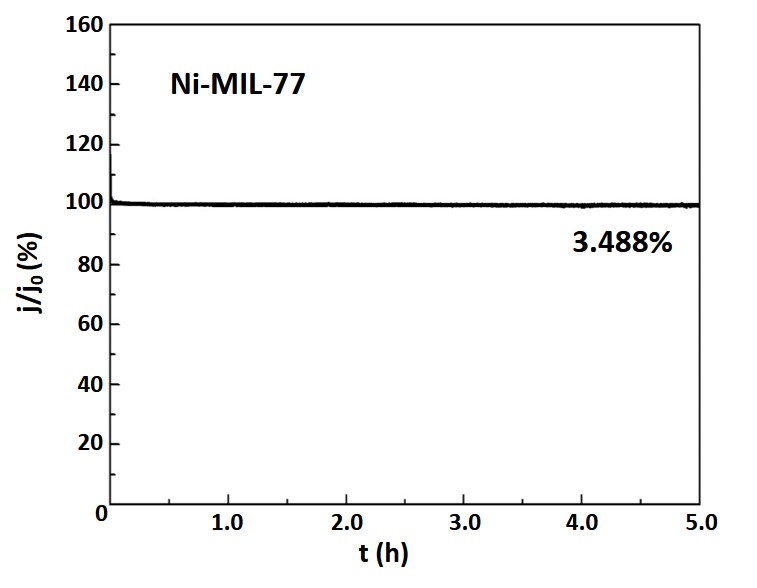
**Figure S10**. a) CVs of the Ni-MOF/GCE electrode in 0.1 M PBS (pH = 7.0) solution containing 5 mM NaNO2 at scan rates from 20 to 200 mV s-1. b) The plots of anodic peak currents to the scan rates. c) Anodic peak potentials versus lg ʋ. It can be found that the anodic peak currents increase linearly with the scan rate and the calibration equation is Ipa (μA) = 0.1695ʋ (mV s-1) + 58.08382 (R2 = 0.955).



**Figure S11**. a) CVs of the Ni/NiO/GCE electrode in 0.1 M PBS solution containing 5 mM NaNO2 with the pH ranging from 4.0 to 8.0, scan rate: 50 mV s-1. b) The anodic peak current against pH.



**Figure S12**. a) CVs of the Ni-MIL-77/GCE electrode in 0.1 M PBS solution containing 5 mM NaNO2 with the pH ranging from 4.0 to 8.0, scan rate: 50 mV s-1. b) The anodic peak current against pH.



**Figure S13**. Stability of Ni-MOF/GCE in 0.1 M PBS (pH=7) with NaNO2 over 5 h.

**Table S1**. Comparison of different measurements for NaNO2 determination.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Electrode** | **Limit of detection (μM)** | **Linear range (μM)** | **Sensitivity** | **Ref.** |
| CNSs | 0.015 | 0.2-400 | 28.91 mA μM-1 cm-2 | (Yallappa et al., 2018) |
| AgNS | 0.031 | 0.1-8 | 580 μA mM-1 cm-2 | (Shivakumar et al., 2017) |
| Co3O4/RGO | 0.14 | 1-380 | 29.5 μA mM-1 cm-2 | (Haldorai et al., 2016) |
| NiO/MWCNTs/CP | 0.25 | 1-100 | 3.53 μA μM-1 cm-2 | (Wan et al., 2017) |
| Fe2O3/rGO | 0.015 | 0.05-780 | 0.204 μA μM-1 cm-2 | (Radhakrishnan et al., 2014) |
| NiCo2CO3(OH)2 | 0.002 | 5-4000 | 1.21 × 10-4 μA mM-1 cm-2 | (Lu et al., 2017) |
| Fe3O4-rGO | 0.3 | 0.5-9563 | 202.5 μA mM-1 cm-2 | (Bharath et al., 2015) |
| Pd/Fe3O4/polyDOPA/RGO | 0.5 | 2.5-6470 | 0.01537 μA μM-1 cm-2 | (Zhao et al., 2017) |
| ERGO/AuNPs/SPCE | 0.13 | 1-6000 | 0.3048 μA μM-1 cm-2 | (Jian et al., 2018) |
| CR-GO | 1.0 | 8.9-167 | 0.0267 A M-1 cm-2 | (Mani et al., 2012) |
| NiFe2O4-CPE | 0.1236 | 0.1-1000 | 7.9617 μA μM-1 cm-2 | (Nithyayini et al., 2019) |
| Cu-MOF/Au | 0.082 | 0.1-4000 | 252 μA mM-1 cm-2 | (Chen et al., 2019) |
| MnO2@g-C3N4 | 0.00123 | 0.01-1520 | 24.1777 μA μM-1 cm-2 | (Keerthi et al., 2019) |
| Co3O4-rGO/CNTs | 0.016 | 0.1-8000 | 0.408 μA μM-1 cm-2 | (Zhao et al., 2019) |
| Ni/NiO NBs | 0.25 | 0.5-1000 | 1.5319 μA mM-1 cm-2 | This work |

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