Electronic Supplementary Information

In Situ Growing MOFs on Ni(OH)$_2$ for Efficient Electrocatalytic Oxidation of 5-Hydroxymethylfurfural

Dongdong Wang,$^a$ Wanbing Gong,*$^a$ Jifang Zhang,$^a$ Guozhong Wang,$^a$ Haimin Zhang$^a$ and Huijun Zhao*$_{a,b}$

$^a$. Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, P. R. China. E-mail: h.zhao@griffith.edu.au, wbgong2021@ustc.edu.cn.

$^b$. Centre for Catalysis and Clean Energy, Gold Coast Campus, Griffith University, Queensland 4222, Australia.
Experimental Section

Chemicals

All reagents were of AR grade and used without further treatment and purification. 5-Hydroxymethylfurfural, 5-hydroxymethyl-2-furancarboxylic acid, 2,5-diformylfuran, 5-formyl-2-furancarboxylic and 2,5-Furandicarboxylic acid were purchased from Aladdin Reagent Company. NiCl$_2$$\cdot$6H$_2$O, thiophene-2,5-dicarboxylate (Tdc), 4, 4’-bipyridine (Bpy), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Regent Co. Ltd. The commercial Ni foam (NF) was obtained from Shanghai Hesen Electric Co. LTD.

Fabrication of Ni(OH)$_2$-NSs/NF

For a typical synthesis, 5 mmol NiCl$_2$$\cdot$6H$_2$O, 10 mmol urea and 4 mmol NH$_4$F were first dissolved in 35 mL deionized water under vigorous stirring. The obtained light green solution was then transferred to a 50 mL Teflon-lined autoclave. A piece of pre-treated NF (1 × 2 cm$^2$) was immersed in the solution, and the autoclave was sealed and heated to 120 °C for 6 h. The obtain Ni(OH)$_2$-NSs/NF was separated from the reaction mixture, washed thoroughly with ethanol and water and dried in oven at 60 °C overnight.

Fabrication of S,N-MOFs@Ni(OH)$_2$-NSs/NF

For a typical synthesis, 296 mg 4, 4’-bipyridine, 280 mg thiophene-2, 5-dicarboxylate and 132 mg NaOH were dissolved in 20 mL deionized water. A piece of the as-synthesized Ni(OH)$_2$-NSs/NF was the immersed in the above solution for 6 h under room temperature to allow the formation of [Ni-(Tdc)(Bpy)]$_n$ MOFs on Ni(OH)$_2$-NSs/NF surface. The resultant S,N-MOFs@Ni(OH)$_2$-NSs/NF was washed thoroughly with ethanol and water and dried in oven at
60 °C overnight.

**Characterizations**

The morphology of samples was characterized by field emission scanning electron microscopy (SU 8020) and transmission electron microscopy (JEOL-2010). X-ray diffraction (XRD) patterns were recorded by a Philips X-Pert Pro diffractometer with a Ni-filtered monochromatic Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). Brunauer-Emmett-Teller (BET) surface areas and pore structure properties were obtained using a surface area and porosity analyzer (Autosorb iQ Station 2). X-ray photoelectron spectra (XPS) were recorded by an ESCALAB 250 system. The thickness of the as-synthesized nanosheets was measured by atomic force microscopy (AFM; PARKNX10). FT-IR spectra were obtained from a Thermo Nicolet NEXUS FI-IR spectrophotometer using a KBr pellet method.

**Electrochemical measurements**

All electrochemical measurements were performed using a two-compartment H-type electrochemical cell with a Nafion membrane separator. All Electrochemical data were recorded by an electrochemical workstation (CHI 760E) using a three-electrode electrochemical system with a $1 \times 1 \text{ cm}^2$ S,N-MOFs@Ni(OH)$_2$-NSs/NF or (Ni(OH)$_2$-NSs/NF or bare NF working electrode, a Hg/HgO reference electrode and a Pt mesh counter electrode in the 1.0 M KOH electrolyte solution with and without 10 mM HMF.

**Products analysis**

The concentrations of HMF and oxidation products were determined by HPLC using a 4.6 mm $\times$ 150 mm Shim-pack GWS 5 μm C-18 column and an ultraviolet-visible detector. HPLC eluents were mixtures of solvents A and B. Solvent A was 5% aqueous ammonium formate
solution and solvent B was methanol. Separation and quantification were performed using an isocratic elution with 60% A and 40% B over 10 min at a flow rate of 0.6 mL min$^{-1}$.

The product yields and faradaic efficiencies (FE) were calculated based on the following equations:

\[
\textit{Yield} (\%) = \frac{\text{Moles of Formed Product}}{\text{Moles of Initial HMF}} \times 100\% \quad (1)
\]

\[
\textit{FE} (\%) = \frac{6F \times (\text{Moles of Formed FDCA})}{Q} \times 100\% \quad (2)
\]

Where, $Q$ is the total transferred charge and $F$ is Faraday constant (96485 C mol$^{-1}$). The quantity of product is determined by HPLC analysis.
Figures and Tables

Fig. S1 (a) FESEM images and (b) AFM image and the corresponding thickness profiles of the as-synthesised Ni(OH)$_2$-NSs/NF.
Fig. S2 (a) SEM image and (b) XRD pattern of the as-synthesised free-standing [Ni-(Tdc)(Bpy)]_n MOFs-NSs. The free-standing [Ni-(Tdc)(Bpy)]_n MOFs NSs were synthesized by adding 228 mg NiCl₂·6H₂O to a 20 mL aqueous solution containing 296 mg of Tdc, 280 mg of Bpy and 132 mg of NaOH.
Fig. S3 XPS spectra of S,N-MOFs@Ni(OH)₂-NSs. (a) Survey spectrum; (b) C 1s spectrum; (c) N 1s spectrum and (d) S 2p spectrum.
Fig. S4 $\text{N}_2$ adsorption-desorption isotherms and corresponding pore size distributions of (a-b) Ni(OH)$_2$-NSs and (c-d) S,N-MOFs@Ni(OH)$_2$-NSs, respectively.
Fig. S5 Nyquist plots of Ni(OH)$_2$-NSs/NF and S,N-MOFs@Ni(OH)$_2$-NSs/NF at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF.
Fig. S6 Self-degradation of HMF (10 mM) in 1.0 M KOH electrolyte in absence of electrocatalyst.
Fig. S7 (a-e) HPLC calibration curves of standard HMF, FDCA, DFF, FFCA and HMFCA samples; (f) HPLC curves from a mixed solution containing HMF, FDCA, DFF, FFCA and HMFCA.
Fig. S8 Chronoamperometric curve and the plot of the transferred charge against reaction time for $S,N$-MOFs@Ni(OH)$_2$-NSs/NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF.
Fig. S9 Anodic chamber solution colour change before and after 2 h HOR catalysed by S,N-MOFs@Ni(OH)$_2$-NSs/NF at 1.4 V (vs. RHE).
Fig. S10 Possible reaction pathways of S,N-MOFs@Ni(OH)$_2$-NSs/NF catalysed HOR.
Fig. S11 Chronoamperometric curves and the plots of the transferred charge against reaction time for S,N-MOFs@Ni(OH)$_2$-NSs/NF catalysed HOR at 1.35, 1.45 and 1.55 V (vs. RHE), respectively.
Fig. S12 (a) Chronoamperometric curve and the plot of the transferred charge against reaction time for NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF; (b) Corresponding HMF and oxidation products concentrations at different reaction times.
**Fig. S13** (a) Chronoamperometric curve and the plot of the transferred charge against reaction time for Ni(OH)$_2$-NSs/NF catalysed HOR at 1.4 V (vs. RHE) in 1.0 M KOH containing 10 mM HMF; (b) Corresponding HMF and oxidation products concentrations at different reaction times.
Fig. S14 Chronoamperometric curves and the plots of the transferred charge against reaction time for Ni(OH)$_2$-NSs/NF catalysed HOR at 1.35, 1.45 and 1.55 V (vs. RHE), respectively.
Fig. S15 FDCA yield and FE for Ni(OH)$_2$-NSs/NF catalysed HOR at different potentials within 2 h in 1.0 M KOH containing 10 mM HMF.
<table>
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<th>Catalysts</th>
<th>C_{HMF} (mM)</th>
<th>Potential (V vs. RHE)</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>FDCA Yield (%)</th>
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References