Supporting Information

Pt/Ni(OH)₂-NiOOH/Pd Multi-Walled Hollow Nanorod Arrays as Superior Electrocatalysts for Formic Acid Electrooxidation

Han Xu,^a Liang-Xin Ding,^b Jin-Xian Feng,^a and Gao-Ren Li*,^a

^aMOE Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

^bSchool of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: ligaoren@mail.sysu.edu.cn



Figure S1. SEM images of (a) ZnO NRAs, (b) ZnO/Pt NRAs, (c) ZnO/Pt/Ni(OH)₂-NiOOH NRAs and (d) ZnO/Pt/Ni(OH)₂-NiOOH/Pd NRAs.



Figure S2. HRTEM image and SAED pattern of the Ni(OH)₂-NiOOH interlayer.



Figure S3. SEM images of (a) Ni(OH)₂-NiOOH/Pt MHNRAs, (b) Ni(OH)₂-NiOOH/Pd MHNRAs, and

(c) Pt/Pd MHNRAs.



Figure S4. XPS spectra of Pt 4*f* of (a) Pt/Ni(OH)₂-NiOOH/Pd MHNRAs and (b) Pt HNRAs.



Figure S5. XPS spectra of Pd 3*d* of (a) Pt/Ni(OH)₂-NiOOH/Pd MHNRAs and (b) Pd HNRAs.



Figure S6. XPS spectra of Ni 2*p* of (a) Pt/Ni(OH)₂-NiOOH/Pd MHNRAs and (b) Ni(OH)₂-NiOOH HNRAs. The magnified XPS spectra of Ni 2*p* of (c) Pt@ Ni(OH)₂-NiOOH@Pd MHNRAs and (d) Ni(OH)₂-NiOOH HNRAs between 854~857 eV.

For XPS spectra of Pt/Ni(OH)₂-NiOOH/Pd MHNRAs and Ni(OH)₂-NiOOH HNRAs as shown in Figure S6a and S6b, respectively, the Ni $2p_{3/2}$ spectrum shows a complex structure and the intense satellite signals are observed. A comparison of the relative areas of the integrated intensity of NiO, Ni(OH)₂ and NiOOH peaks in Figure S6a and S6b indicates that the main compounds are Ni hydroxides (Ni(OH)₂-NiOOH) and a small quantity of NiO are found in the Pt/Ni(OH)₂-NiOOH/Pd MHNRAs. Compared with Ni(OH)₂-NiOOH HNRAs, the Pt/Ni(OH)₂-NiOOH/Pd MHNRAs exhibit a much higher content of Ni(OH)₂-NiOOH.



Figure S7. (a) CVs of the Pt/Ni(OH)₂-NiOOH/Pd MHNRAS, Ni(OH)₂-NiOOH/Pt MHNRAS and Ni(OH)₂-NiOOH/Pd MHNRAS in the deaerated solution of 0.5 M H₂SO₄ at 20 mV s⁻¹; (b) CVs of the Pt/Ni(OH)₂-NiOOH/Pd MHNRAS, Ni(OH)₂-NiOOH/Pt MHNRAS and Ni(OH)₂-NiOOH/Pd MHNRAS electrocatalysts in solution of 0.5 M HCOOH+0.5 M H₂SO₄ at 100 mV s⁻¹; (c) CVs of the Pt/Ni(OH)₂ - NiOOH/Pd MHNRAS, Pt/Pd MHNRAS, and commercial Pt/C, Pd/C, PtRu/C catalysts in solution of 0.5 M HCOOH+0.5 M H₂SO₄ at 100 mV s⁻¹; (d) CO stripping voltammograms on the Pt/Ni(OH)₂-NiOOH/Pd MHNRAS, Ni(OH)₂-NiOOH/Pt MHNRAS and Ni(OH)₂-NiOOH/Pd MHNRAS performed in solution of 0.5 M H₂SO₄ at 20 mV s⁻¹.



Figure S8. The backward scan peaks of CVs between -0.2 and 1.0 V for $Pt/Ni(OH)_2$ -NiOOH/Pd MHNRAs, Pt/Pd MHNRAs, and commercial Pt/C, Pd/C, PtRu/C catalysts in solution of 0.5 M HCOOH +0.5 M H₂SO₄ at 100 mV s⁻¹.



Figure S9. Nyquist plots of the Pt/Ni(OH)₂-NiOOH/Pd MHNRAs and Pt/Pd MHNRAs in solution of 0.5 M HCOOH+0.5 M H₂SO₄.



Figure S10. The comparisons of the maximum specific peak current densities after 1st cycle and the maximum specific peak current densities after 500th cycle of the Pt/Ni(OH)₂-NiOOH/Pd MHNRAs, Ni(OH)₂-NiOOH/Pt MHNRAs and Ni(OH)₂-NiOOH/Pd MHNRAs electrocatalysts.



Figure S11. SEM image of Pt/Ni(OH)₂-NiOOH/Pd MHNRAs after 500 cycles.