**Electrochemical co-deposited Pd-CoOx coating for efficient synergistic electrocatalytic reduction of nitrate to ammonia**

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**Supplementary Information**

1. Figure S1. LSV curves of Pd-CoOx deposited at different potentials and with different times
2. Figure S2. Calibration curves of NH4+, NO2-, NH4+ obtained by UV method and IC methods, and NH3 yields of Pd-CoOx compared to those under conditions of no catalyst and no voltage
3. Figure S3. NO2- yields of Pd, CoOx and Pd-CoOx catalysts at different potentials
4. Figure S4. SEM and TEM images of Pd-CoOx before reaction and after reaction
5. Figure S5. Pd 3d and Co 2p XPS spectra of Pd-CoOx before and after reaction
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8. Figure S8. Elemental contents of catalysts with different ratios of Pd and Co by ICP
9. Figure S9 NH3 yields of Pd, Pd0.93Co0.07, Pd0.86Co0.14 and Pd0.5Co0.5 in 1M NaOH and 0.1M NaNO3
10. Figure S10. In situ Raman spectra over time of Pd and Pd-CoOx catalysts
11. Table S1. Comparation of NIRR performance of Pd-CoOx with reported catalysts

**Supporting Figures**



Figure S1. (a) LSV curves of Pd-CoOx deposited at different potentials and (b) with different times.



Figure S2. (a) calibration curve of NH4+ obtained by UV method, (b) calibration curve of NO2- obtained by UV method, (c) calibration curve of NO3- obtained by UV method, (d) calibration curve of NH4+ obtained by IC method, (e) calibration curve of NO2- obtained by IC method, (f) calibration curve of NO3- obtained by IC method, (g) UV response and (h) NH3 yield of Pd-CoOx compared to those under conditions of no catalyst and no voltage, (i) comparation of NH3 yield obtained by UV and IC methods.



Figure S3. NO2- yield of Pd, CoOx and Pd-CoOx at different potentials from 0 V to -0.4 V *vs.* RHE.

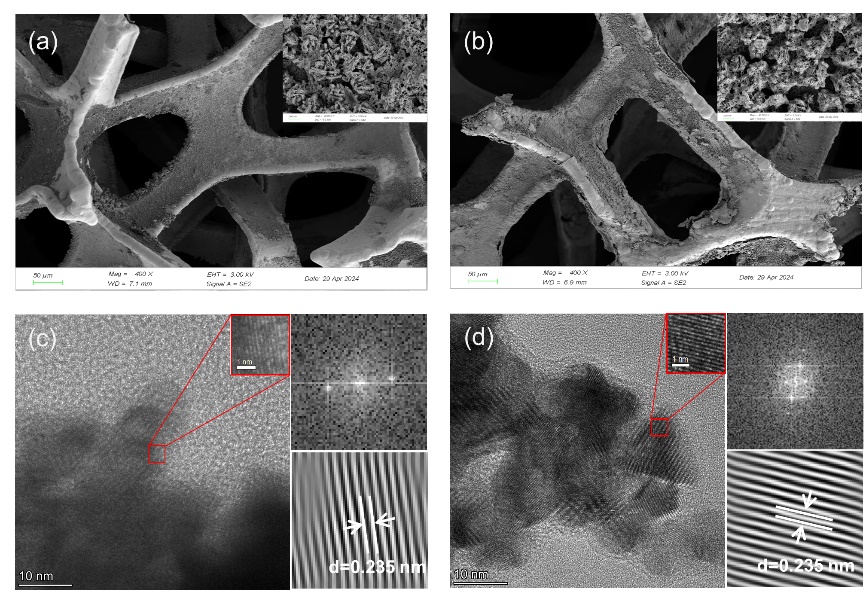


Figure S4. (a)SEM images of Pd-CoOx before reaction and (b) after reaction, (c) TEM images of Pd-CoOx before reaction and (d) after reaction.



Figure S5. (a) Pd 3d XPS spectra of Pd-CoOx before and after reaction, (b) Co 2p XPS spectra of Pd-CoOx before and after reaction.



Figure S6. CV curves at different scan rates from 10 mV\*s-1 to 200 mV\*s-1 of Pd, CoOx and Pd-CoOx.



Figure S7. Bode plots of Pd, CoOx and Pd-CoOx.



Figure S8. Elemental contents of deposited catalysts with different ratios of PdCl2 and CoCl2 in deposition solution by ICP.



Figure S9. NH3 yields of Pd, Pd0.93Co0.07, Pd0.86Co0.14 and Pd0.5Co0.5 at a constant current density of 250 mA\*cm-2in 1MNaOH and 0.1M NaNO3.



Figure S10. (a) In situ Raman spectra over time at a constant current density of 1 mA\*cm-2 in 1M NaOH and 0.1M NaNO3 of Pd and (b) Pd-CoOx.

**Supporting Tables**

Table S1. Comparation of NIRR performance of Pd-CoOx with reported catalysts

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalyst | NH3 yield  (mg\*h-1\*cm-2) | FE (%) | Potential  (V *vs.* RHE) | Electrolyte | Ref. |
| Pd crystalline | 9.3 | 79.9 | -0.7 | 0.1M Na2SO4 + 0.1M NaNO3 | 1 |
| Pd/TiO2 | 1.1 | 92.1 | -0.8 | 0.1M Na2SO4 + 0.25M NaNO3 | 2 |
| Co/CC | 10.2 | 93.4 | -0.8 | 0.1M NaOH + 0.1M NaNO3 | 3 |
| Cu2O | 0.37 | 82.3 | -0.6 | 0.1M Na2SO4 + 50 ppm NaNO3 | 4 |
| Co/TiO2 | 3.8 | 97.4 | -0.7 | 1M PBS + 0.4M NaNO3 | 5 |
| Co3O4-Ov | 13.2 | 95.5 | -0.8 | 0.1M NaOH + 0.1M NaNO3 | 6 |
| NiCo2O4/CC | 17.5 | 99 | -0.6 | 0.1M NaOH + 0.1M NaNO3 | 7 |
| CoMn2O4/CC | 11.2 | 98.6 | -1 | 0.1M PBS + 0.1M NaNO3 | 8 |
| CoP/TiO2 | 8.5 | 95 | -0.3 | 0.1M NaOH + 0.1M NaNO3 | 9 |
| Cu-N-C | 0.18 | 94 | -1.25 | 0.5M Na2SO4 + 50 ppm NaNO3 | 10 |
| Co2AlO4/CC | 10.8 | 98.3 | -0.9 | 0.1M NaOH + 0.1M NaNO3 | 11 |
| NiFe2O4/CC | 5 | 95.9 | -0.5 | 0.1M NaOH + 20mM NaNO3 | 12 |
| Fe3C/NC | 8.1 | 96.7 | -0.5 | 1M KOH + 75mM KNO3 | 13 |
| SAC-Ru | 19.9 | 96 | -0.8 | 1 M KOH and 1M KNO3 | 14 |
| Nano-Ag | 16.4 | 96.4 | -0.35 | 1M KOH + 14.3mM KNO3 | 15 |
| our work | 30.2 | 99.8 | -0.4 |  |  |

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