Supporting Information

Co – Doped Porous Niobium Nitride Nanogrid as Effective Oxygen Reduction Catalyst

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Fig. S1 shows the XRD patterns of the synthesized NbN and Nb$_{0.95}$M$_{0.05}$Ns. After the nitridation process, only the fcc Nb$_4$N$_5$ phase could be observed for all of the Nb$_{0.95}$M$_{0.05}$N, and the locations of the diffraction peaks were almost identical to those of NbN NPs. Furthermore, no signals corresponding to a single metallic phase or to the oxide or nitride phases of the doping elements were detected, suggesting that the Nb$_{0.95}$M$_{0.05}$N were formed as a highly pure, single-phase solid solution.

Using the Scherrer equation, we estimated the average particle sizes of the Nb$_{0.95}$M$_{0.05}$N to be 18.7, 19.8, 19.6, 17.5 and 20.2 nm for NbN, Nb$_{0.95}$Ni$_{0.05}$N, Nb$_{0.95}$Co$_{0.05}$N, Nb$_{0.95}$Cu$_{0.05}$N and Nb$_{0.95}$Zn$_{0.05}$N, respectively.

![Fig. S1 XRD pattern of Nb$_{0.95}$M$_{0.05}$N annealed at 750°C](image)

Fig. S1 XRD pattern of Nb$_{0.95}$M$_{0.05}$N annealed at 750°C

![Fig. S2](image)

Fig. S2 (a) XRD pattern and (b) TEM image of Nb$_{0.95}$Co$_{0.05}$N nanoparticle prepared by chemical
Fig. S3 Linear sweep voltammetry curves of Nb$_{0.95}$Co$_{0.05}$N nanoparticle and Nb$_{0.95}$Co$_{0.05}$N nanogrid, calculated by subtracting N$_2$-saturated solution from O$_2$-saturated solution at a rotation speed of 1600 rpm.

Fig. S4 CVs of (a) NbN, (b) Nb$_{0.95}$Co$_{0.05}$N, in N$_2$-saturated 0.1 M KOH solution at a scan rate of 50mV s$^{-1}$. 
To well understand the mechanism of doping effect, we conducted O\textsubscript{2}-TPD tests for Nb\textsubscript{0.95}Co\textsubscript{0.05}N and NbN. As presented in Figure S6-a, both NbN and Nb\textsubscript{0.95}Co\textsubscript{0.05}N showed two strong desorption peaks in the same temperature areas. The left peaks of the two catalysts around 92 \degree C were almost coincidence, which corresponds to desorption of free oxygen. In comparison to NbN, the strong desorption peaks of Nb\textsubscript{0.95}Co\textsubscript{0.05}N around 300\degree C showed a slightly positive shift, indicating that doping with Co strengthened the adsorption of oxygen on the catalyst. And this is probably the reason for the enhanced performance. At a deeper level, the experiment results of O\textsubscript{2}-TPD might caused by the change of the electronic structures of Nb, which we have observed in XPS results. In addition, the XRD pattern of Nb\textsubscript{0.95}Co\textsubscript{0.05}N after the O\textsubscript{2}-TPD test (Figure S-6b) suggests that these peaks were not derived from the self-decomposition of Nb\textsubscript{0.95}Co\textsubscript{0.05}N.
Methanol tolerance properties of the Nb$_{0.95}$Co$_{0.05}$N were investigated using LSV measurements in the presence of 0.1 M methanol. As shown in Figure S7, Nb$_{0.95}$Co$_{0.05}$N exhibited little activity loss indicating an excellent tolerance to methanol.

Table S1 lists the compositions of several catalysts as measured by XPS. Clearly, the actual ratio of Co/Nb in Nb$_{0.95}$Co$_{0.05}$N is higher than the values obtained from ICP. This deviation suggests the surface enrichment of cobalt in Nb$_{0.95}$Co$_{0.05}$N nanogrid. The presence of O atoms is because the catalysts were exposed in the air for a while.
### Table S1 The atomic compositions of NbN and Nb$_{0.95}$Co$_{0.05}$N

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NbN</th>
<th>Nb$<em>{0.95}$Co$</em>{0.05}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>42.62%</td>
<td>39.12%</td>
</tr>
<tr>
<td>N</td>
<td>28.76%</td>
<td>29.71%</td>
</tr>
<tr>
<td>Nb</td>
<td>28.62%</td>
<td>26.08%</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>5.08%</td>
</tr>
<tr>
<td>Co/Nb</td>
<td></td>
<td>19.48%</td>
</tr>
</tbody>
</table>

The theoretical value of Co/Nb is 5.3%