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Supporting Information

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

Haibo Tang, Xinlong Tian, Junming Luo, Jianhuang Zeng, Yingwei Li, Huiyu Song*, Shijun Liao*

The Key Laboratory of Fuel Cell Technology of Guangdong Province & The Key Laboratory of New Energy Technology of Guangdong Universities, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China

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_4N_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.

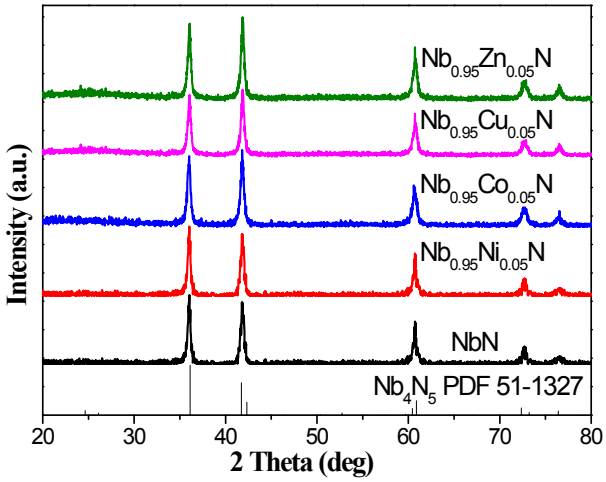

Fig. S1 XRD pattern of $Nb_{0.95}M_{0.05}N$ annealed at 750℃

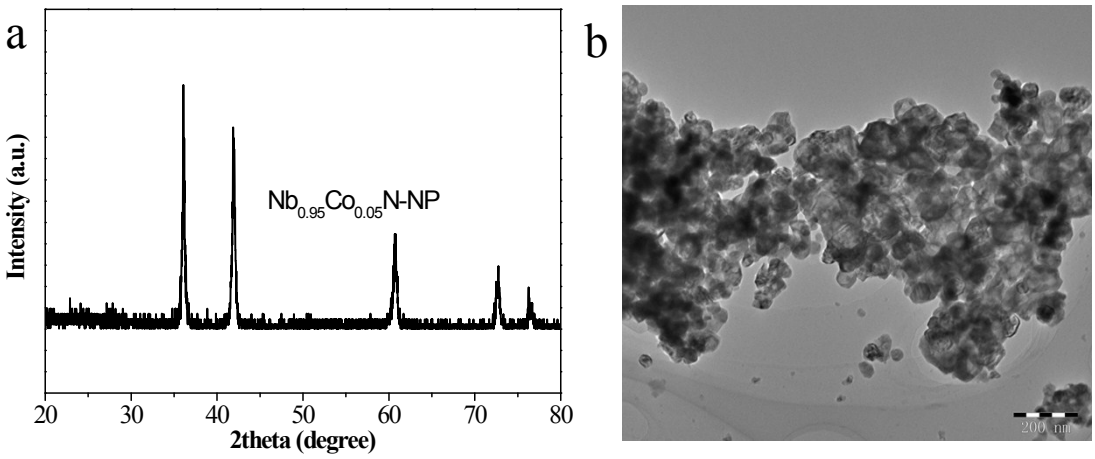

Fig. S2 (a) XRD pattern and (b) TEM image of $Nb_{0.95}Co_{0.05}N$ nanoparticle prepared by chemical

precipitation.

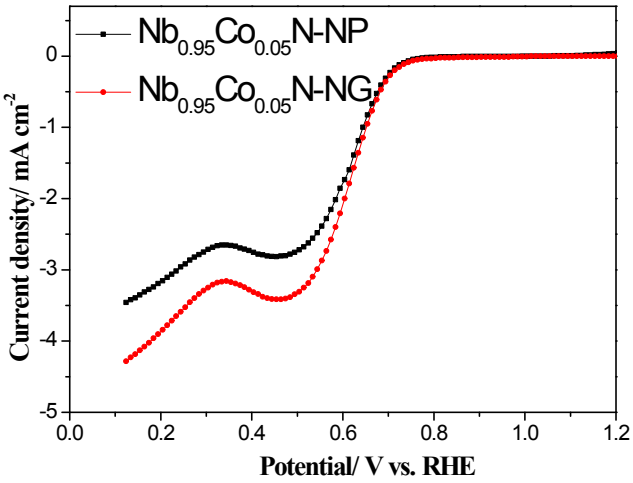

Fig. S3 Linear sweep voltammetry curves of $Nb_{0.95}Co_{0.05}N$ nanoparticle and $Nb_{0.95}Co_{0.05}N$ nanogrid, calculated by subtracting N_2-saturated solution from O_2-saturated solution at a rotation speed of 1600 rpm.

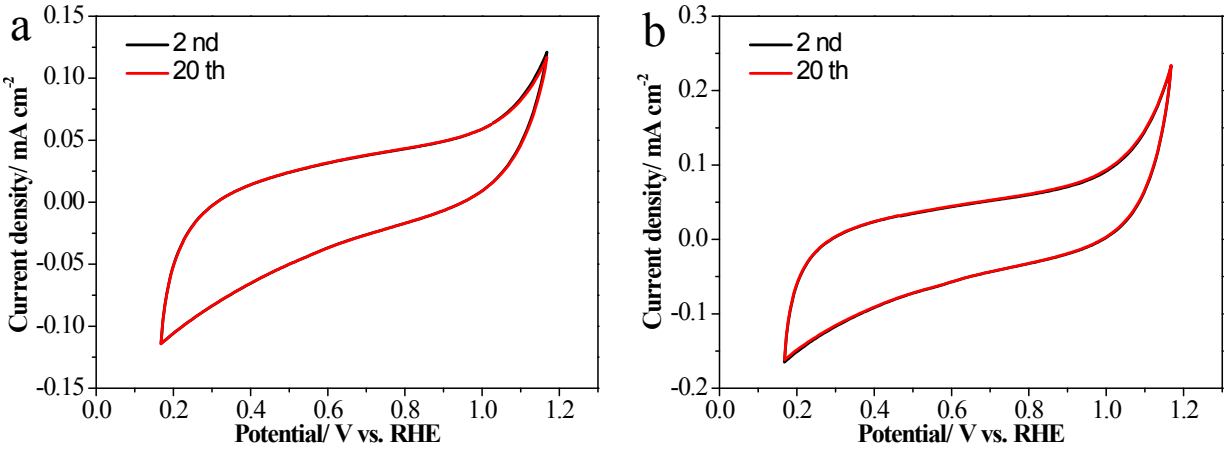

Fig. S4 CVs of (a) NbN, (b) $Nb_{0.95}Co_{0.05}N$, in N_2-saturated 0.1 M KOH solution at a scan rate of 50mV s^{-1}.

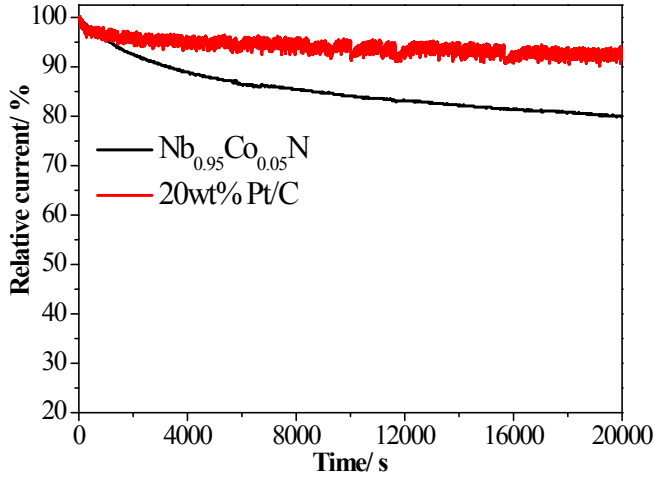

Fig. S5 Catalytic stability of $Nb_{0.95}Co_{0.05}N$ and JM 20% Pt/C catalyst polarized at 0.521 V (vs RHE) during 20000 s in O_2-saturated 0.1 M KOH solution at a rotation rate of 900 rpm.

To well understand the mechanism of doping effect, we conducted O_2-TPD tests for $Nb_{0.95}Co_{0.05}N$ and NbN. As presented in Figure S6-a, both NbN and $Nb_{0.95}Co_{0.05}N$ showed two strong desorption peaks in the same temperature areas. The left peaks of the two catalysts around 92 ºC were almost coincidence, which corresponds to desorption of free oxygen. In comparison to NbN, the strong desorption peaks of $Nb_{0.95}Co_{0.05}N$ around 300ºC 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_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 $Nb_{0.95}Co_{0.05}N$ after the O_2-TPD test (Figure S-6b) suggests that these peaks were not derived from the self-decomposition of $Nb_{0.95}Co_{0.05}N$.

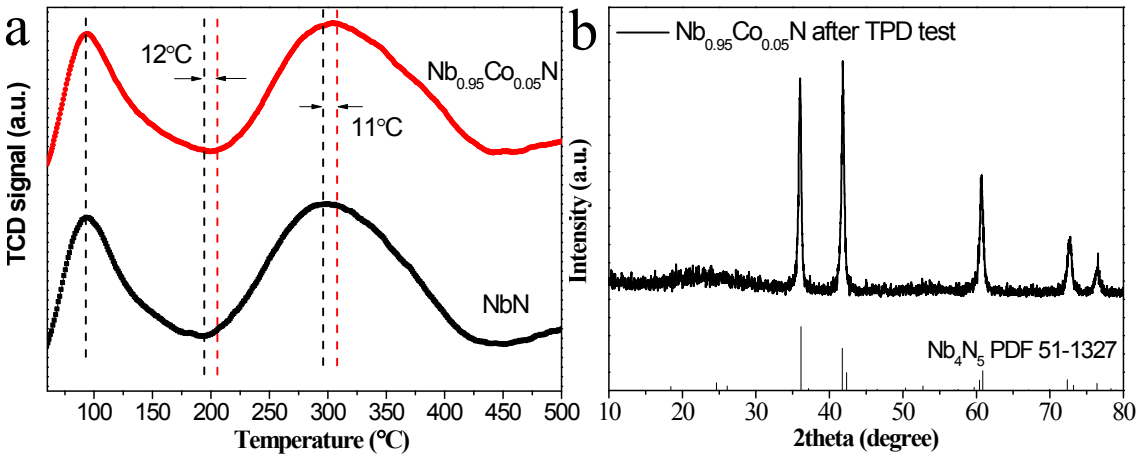

Fig. S6 (a) O_2-TPD curves of NbN and $Nb_{0.95}Co_{0.05}N$ **(b)** XRD pattern of $Nb_{0.95}Co_{0.05}N$ after the O_2-TPD test

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.

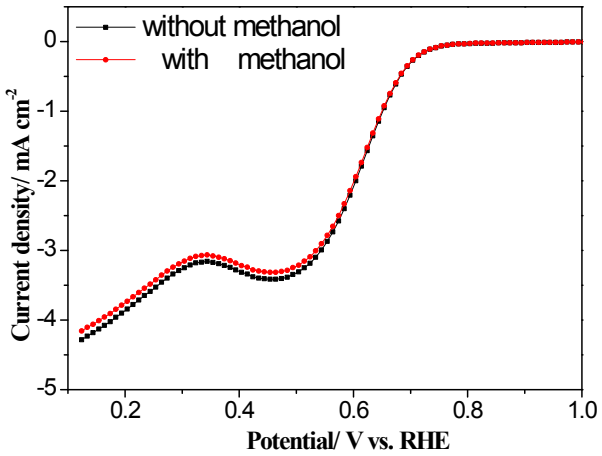

Fig. S7 LSV result of $Nb_{0.95}Co_{0.05}N$ to test methanol tolerance

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 $Nb_{0.95}Co_{0.05}N$

Catalysts	NbN	$Nb_{0.95}Co_{0.05}N$
O	42.62%	39.12%
N	28.76%	29.71%
Nb	28.62%	26.08%
Co		5.08%
Co/Nb		19.48%
The theoretical value of Co/Nb is 5.3%		