Supporting Information

Molybdenum nitride electrocatalyst for hydrogen evolution more efficient than platinum/carbon: Mo$_2$N/CeO$_2$@nickel foam

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The XRD patterns of CeO$_2$@NF and (CeO$_2$ precursor}@NF (Figure S1a of the supporting information, SI) show the diffraction peaks of CeO$_2$ (JCPDS no. 1-800) and Ce$_2$(CO$_3$)$_2$(OH)$_2$·H$_2$O (JCPDS no. 46-369), in addition to those of the NF substrate, indicating that the CeO$_2$ precursors consist of mixtures. The XRD pattern of CeO$_2$@NF shows that the nitridation at 500 ºC transforms the CeO$_2$ precursors to CeO$_2$, which indicating that this low-temperature nitridation does not change the composition of CeO$_2$, and the Ce$_2$(CO$_3$)$_2$(OH)$_2$·H$_2$O is also transformed to CeO$_2$. In the XRD patterns of (Mo$_2$N precursor]@NF, Mo$_2$N@NF and Mo$_2$N powders (Figure S1b), only weak XRD peaks corresponding to Mo$_2$N (JCPDS NO. 25-1366) can be observed indicating the poor crystallinity of Mo$_2$N. Only the peaks of NF are seen in (Mo$_2$N precursor]@NF and Mo$_2$N@NF suggesting low content and low crystallinity of Mo$_2$N precursor or Mo$_2$N. The SEM images of (CeO$_2$ precursor]@NF (Figure S1c) and the CeO$_2$@NF (Figure S1d) show that the NF is covered with a layer of the precursor and CeO$_2$, respectively. The SEM images of (Mo$_2$N precursor]@NF (Figure S1e) and Mo$_2$N@NF (Figure S1f) show that the NF covered with a certain layer, but the nature of these layers is unclear.
Figure S1. XRD patterns (a) and SEM images of CeO$_2$ precursors (c) and CeO$_2$@NF (d). XRD patterns (b) and SEM images of (Mo$_2$N precursor)@NF (e) and Mo$_2$N@NF (f).
Figure S2. (a, b) XRD patterns of (Mo$_2$N precursor)/(CeO$_2$ precursor)@NF and Mo$_2$N/CeO$_2$@NF-0.05.

Figure S3. (a) Polarization curves and (b) Tafel slopes of Mo$_2$N/CeO$_2$@NF-n (n = 0.02, 0.04, 0.05, 0.06) toward the HER.

Figure S4. (a, b) SEM images of Mo$_2$N/CeO$_2$@NF-0.04 and Mo$_2$N/CeO$_2$@NF-0.06.
Figure S5. (a-d) Cyclic voltammographs with the scan rate from 5 to 100 mV/s for Mo$_2$N/CeO$_2$@NF-n (n = 0.02, 0.04, 0.05, 0.06) in the region of 0.1 - 0.2 V vs. RHE in 1 M KOH.

Figure S6. XPS spectra of the (a) Mo 3d, (b) Ce 3d of Mo$_2$N/CeO$_2$@NF-n (n = 0.02, 0.04, 0.05, 0.06)

Figure S7. Durability test of HER for Mo$_2$N/CeO$_2$@NF-0.05 for 100 h.
We explore the cations of Mo$_2$N/CeO$_2$@NF-0.05 change their valence states during the HER by comparing the XPS spectra taken before and after the HER for 24 h. The Ce 3d XPS spectra (Figure S9a) show that the reaction decreases the concentration of Ce$^{3+}$ while increasing that of Ce$^{4+}$, implying a decrease in the number of oxygen vacancies during the reaction. This implication is also supported by the Mo 3d XPS spectra (Figure S9b); the reaction for 24 h decreases the concentration of the Mo$^{3+}$ ions (from 40.8 to 12.5 %), but increases those of the Mo$^{4+}$ and Mo$^{6+}$ ions (from 20.5 and 38.7 % to 30 and 57.5 %, respectively). Since the activity of Mo$_2$N/CeO$_2$@NF-0.05 for the HER is hardly diminished even well beyond 24 h of the reaction, where the concentration of Mo$^{3+}$ ions is low, the above finding indicates that the presence of Mo$^{4+}$/Mo$^{6+}$ valence states is primarily responsible for the HER. The O 1s XPS peaks of the O-M (M: Mo and Ce) bond moves towards a higher binding energy (Figure S9c), which is consistent with the finding that the reaction increases the amount of Mo$^{6+}$ and Ce$^{4+}$. This is consistent with the finding that the average oxidation state of Mo and Ce are increased by the reaction. The O 1s peak of the OH$^{-}$ (531.9 eV) indicates the presence of adsorbed water on the surface of catalyst. The N 1s peak of the N-Mo bond is shifted to a higher binding energy by the reaction (Figure S9d), and so is the Mo 3p$_{3/2}$ peak. This is consistent with the finding that the average oxidation state of Mo is increased by the reaction. In addition, the intensities
of the N 1s peak and the Mo 3p\textsubscript{3/2} peak decrease after the reaction, indicating some loss of Mo\textsubscript{2}N on the surface that were in contact with the solution during the reaction.

Figure S10. XPS spectra of (a) Ce 3d, (b) Mo 3d, (c) O 1s and (d) N 1s-Mo 3p\textsubscript{3/2} of Mo\textsubscript{2}N/CeO\textsubscript{2}@NF-0.05 before and after the stability test for 24 h.
**Figure S11.** The atomic structures of water adsorption/dissociation and the hydrogen intermediates adsorption on (a) Mo$_2$N (200) surface, (b) CeO$_2$ (111) surface and (c) Mo$_2$N/CeO$_2$(111), where the blue, orange, kelly and red balls represent Mo, N, Ce and O atoms.
Table S1. Comparison of HER activity of Mo$_2$N/CeO$_2$@NF-0.05 electrode with other reported HER catalysts.

<table>
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<th>Catalysts</th>
<th>$\eta$ at 10 mA/cm$^2$ (mV vs RHE)</th>
<th>Electrolyte (pH)</th>
<th>Scan rate (mV/s)</th>
<th>Ref.</th>
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References


