Understanding the Mechanism of Hydrogenated NiCo$_2$O$_4$Nanograss Supported on Ni foam for Enhanced Performance Supercapacitors

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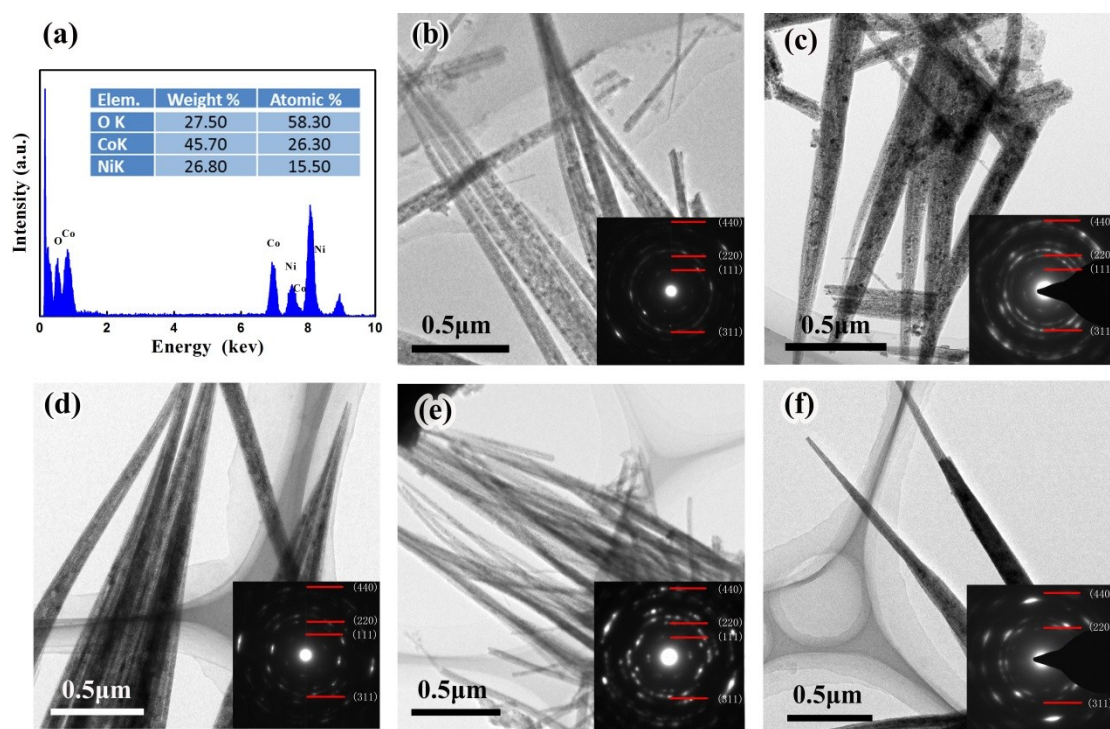Fig S1 Structure and morphology of pristine NiCo$_2$O$_4$ samples and H-NiCo$_2$O$_4$ samples. (a) pristine samples, (b, c, f , e) H-NiCo$_2$O$_4$ 1h, 2h, 3h, 4h, (f) XRD patterns of pristine NiCo$_2$O$_4$ samples and H-NiCo$_2$O$_4$ samples, from the bottom to the top is pristine, 1h, 2h, 3h and 4h in turn.

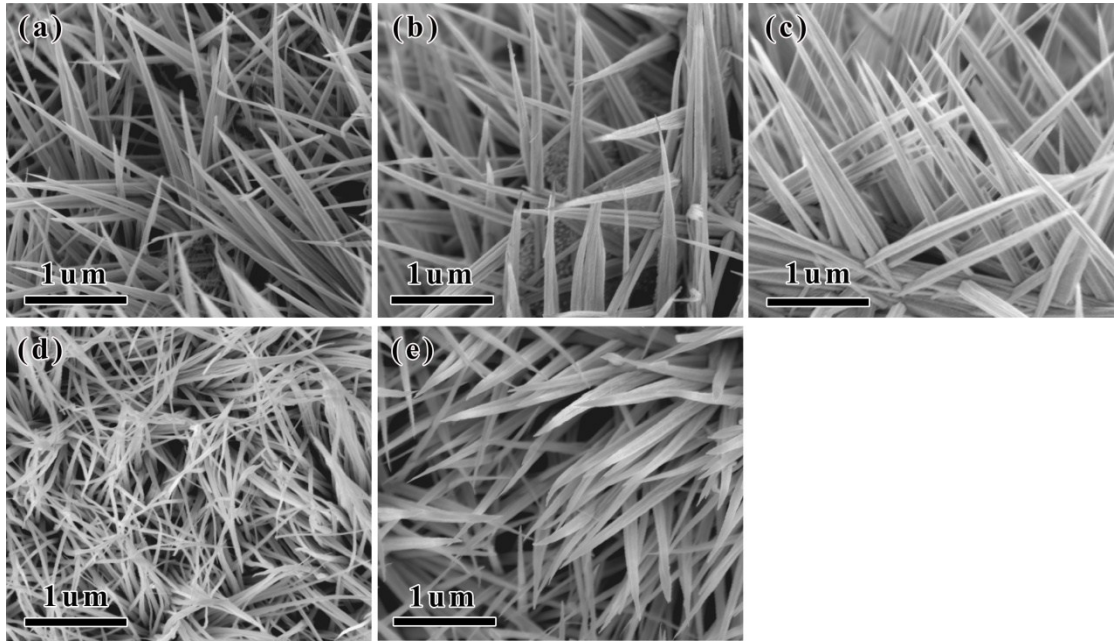Fig S2 High resolution SEM images of pristine NiCo$_2$O$_4$ samples and H-NiCo$_2$O$_4$ samples. From (a)

to (e) corresponding to the pristine, 1 h, 2h, 3h and 4h in turn.
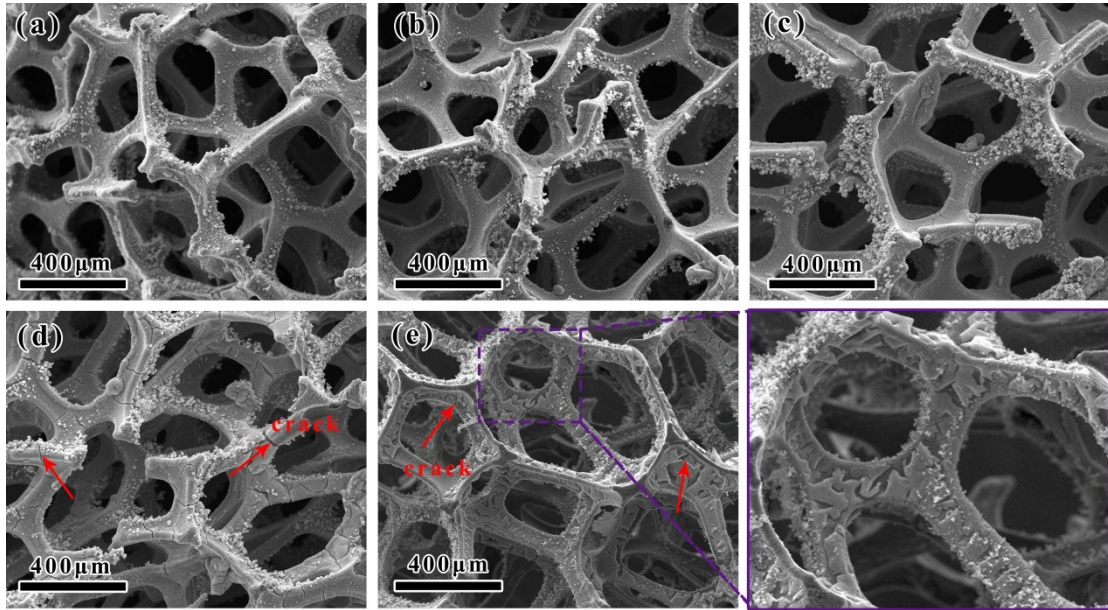
Fig. S3 SEM images of pristine NiCo$_2$O$_4$ samples and H-NiCo$_2$O$_4$ samples. From (a) to (e) corresponding to the pristine, 1h, 2h, 3h and 4h in turn. It can be obviously observed that more cracks appeared in Fig. d and e.
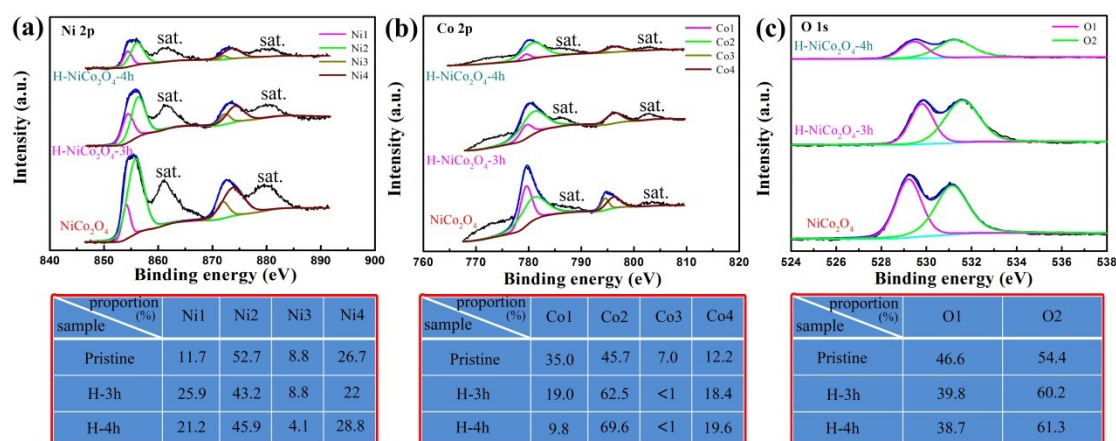
Fig.S4 XPS spectra comparison of pristine $NiCo_2O_4$, H-$NiCo_2O_4$ 3h and H-$NiCo_2O_4$ 4 h samples.(a) Ni 2p, (b) Co 2p, (c) O 1s.

XPS survey spectra of both pristine $NiCo_2O_4$ and hydrogenated $NiCo_2O_4$-3h nanograss are described in Fig.S4. All of the spectra were calibrated with the C 1s peak at 284.8 eV. Fig S4a-c shows the XPS spectra and the corresponding compositions of Ni 2p, Co 2p, O 1s of the initial sample and the hydrogenated sample. As shown in Fig. S4a, compared with the pristine sample, each segment changes slightly after hydrogenation, which may be consistent with Co 2p spectra change. Because of little content of Ni element, the change of Ni valance state only can describe the formation of oxygen vacancies qualitatively. In the Fig. S4b, the spectra are composed of two spin-orbit doublets [Co1, Co3] (Co^{3+}) and [Co2, Co4](Co^{2+}). The proportions of [Co2, Co4](Co^{2+}) in the sample of the H-$NiCo_2O_4$3h and H-$NiCo_2O_4$ 4h increased 62.5% and 69.6% with reference to the pristine state (45.7%), suggesting there were more and more Co^{2+} ion in the sample after hydrogenation. The result suggests that a larger number of cobalt cations reduced from the Co^{3+} to the Co^{2+} spectra.[1] The O1s spectra for pristine and hydrogenated sample were shown in Fig S4c. Both samples exhibit two

oxygen contributions donated as O1 and O2, associated with the typical of metal-oxygen bonds in $NiCo_2O_4$,[3,4] substitution of oxygen atoms at the surface by hydroxyl groups.[5] Compared with the pristine $NiCo_2O_4$ nanograss, the O^{2-} peaks shifted from 529.2 eV to 529.9 eV(3h) and 529.4 eV (4 h), which means O^{2-} ions have different environment in hydrogenated sample. The proportion of the O1 (O^{2-} state) for the hydrogenated sample decreases from 46.6% (pristine) to 39.8% (3 h) and 38.7% (4 h). Nevertheless, the proportion of O2 increased from 54.4% (pristine) to 60.2% (3h) and 61.3% (4h), indicating that more hydroxyl groups and likely more oxygen vacancies were created in the sample after hydrogenation. In a word, as the result shown in Fig.S4, the density of oxygen vacancies increased with the hydrogenated time extension.

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3 T. Choudhury, S. O. Saied, J. L. Sullivan, A. M. Abbot, *J. Phys. D: Appl. Phys.*1989, 22, 1185.

4 J. F. Marco, J. R. Gancedo, M. Gracia, *J. Solid State Chem.* 2000, 153, 74 .

5 Y. E. Roginskaya, O. V. Morozova, E. N. Lubnin, Y. E. Ulitina, G. V. Lopukhova and S. Trasatti, *Langmuir* 1997, 13, 4621.

The calculation of mass loading

The ICP analysis was used to calculate the mass loading on the Ni foam. In a typical procedure, the $NiCo_2O_4$ combined with Ni foam obtained after the synthesis reaction was dissolved in 25 ml of concentrated nitric acid, and diluted with deionized water to 250 ml. Then the samples were analyzed by ICP-AES. In the ICP-AES analysis, the content of cobalt was tested. As the content of Cobalt in the $NiCo_2O_4$ is constant, the mass loading of $NiCo_2O_4$ on the Ni foam could be calculated through the Equation (1). The results were shown in the table S1.

$$M = a \times 0.250 \text{ (L)} \times M_{NiCo2O4} / 2M_{Co} \tag{1}$$

Where M (mg) represents the mass loading of $NiCo_2O_4$, a (ppm) represents the content of cobalt, $M_{NiCo2O4}$ represents the molar mass of $NiCo_2O_4$, M_{Co} represents the molar mass of cobalt.

Table S1. The Cobalt content of the samples.

No	Content of cobalt (ppm)	Mass loading (mg)
1	0	0
2	5.2	2.64
3	5.1	2.61
4	4.6	2.37
5	5.0	2.58
6	4.2	2.8
Average	4.82	2.6

To eliminate the influence of Nickel foam that may import the Cobalt into the solution,

we have tested the pure Nickel foam (No 1) to detect the content of Cobalt. Fortunately, the content of Cobalt in Nickel foam is 0, showing that the Nickel foam did not import the impurity. Through the calculation, we got that the mass loading of $NiCo_2O_4$ was 2.6 mg.

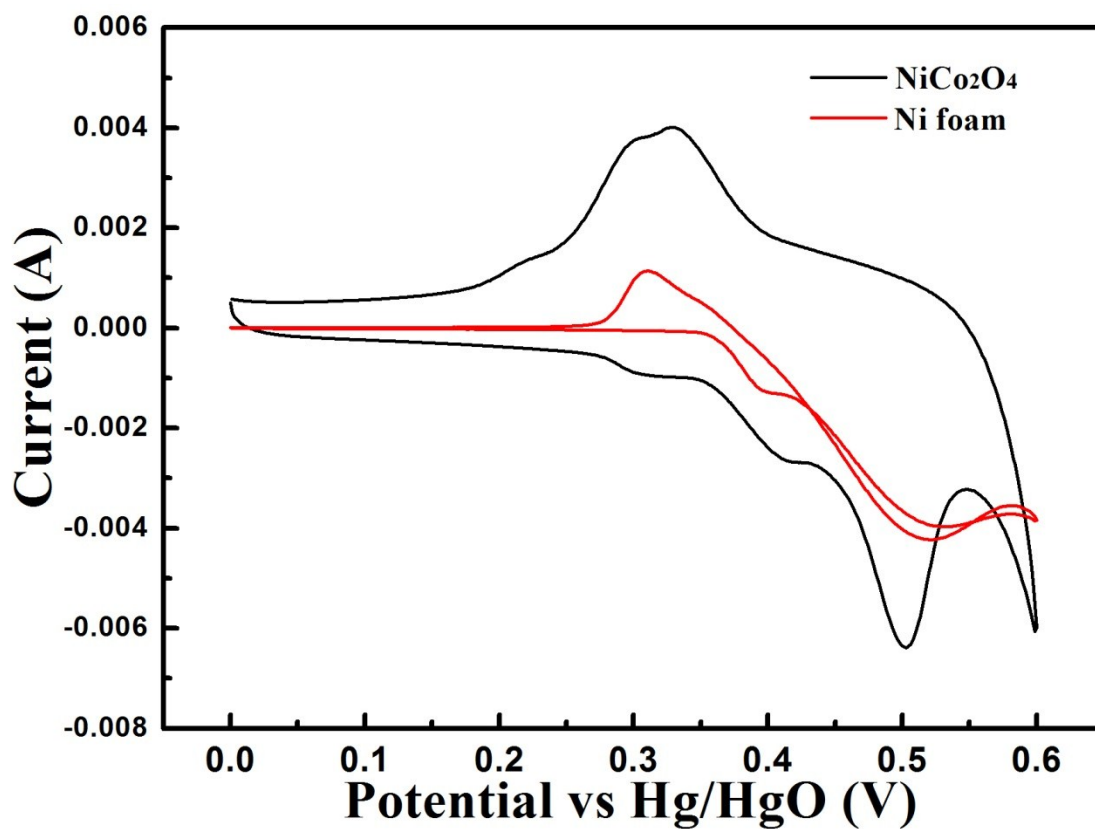Fig.S5. CV curves of Ni foam and NiCo$_2$O$_4$.

The CV curves of the initial NiCo$_2$O$_4$ and Ni foam are shown in Fig. S5 at a scanning rate of 5 mVs^{-1}. It is notable that the enclosed separation area of NiCo$_2$O$_4$ is much greater than Ni foam, indicating that the performance of Ni foam has little influence on the electrochemical performance of NiCo$_2$O$_4$ and even H-NiCo$_2$O$_4$.
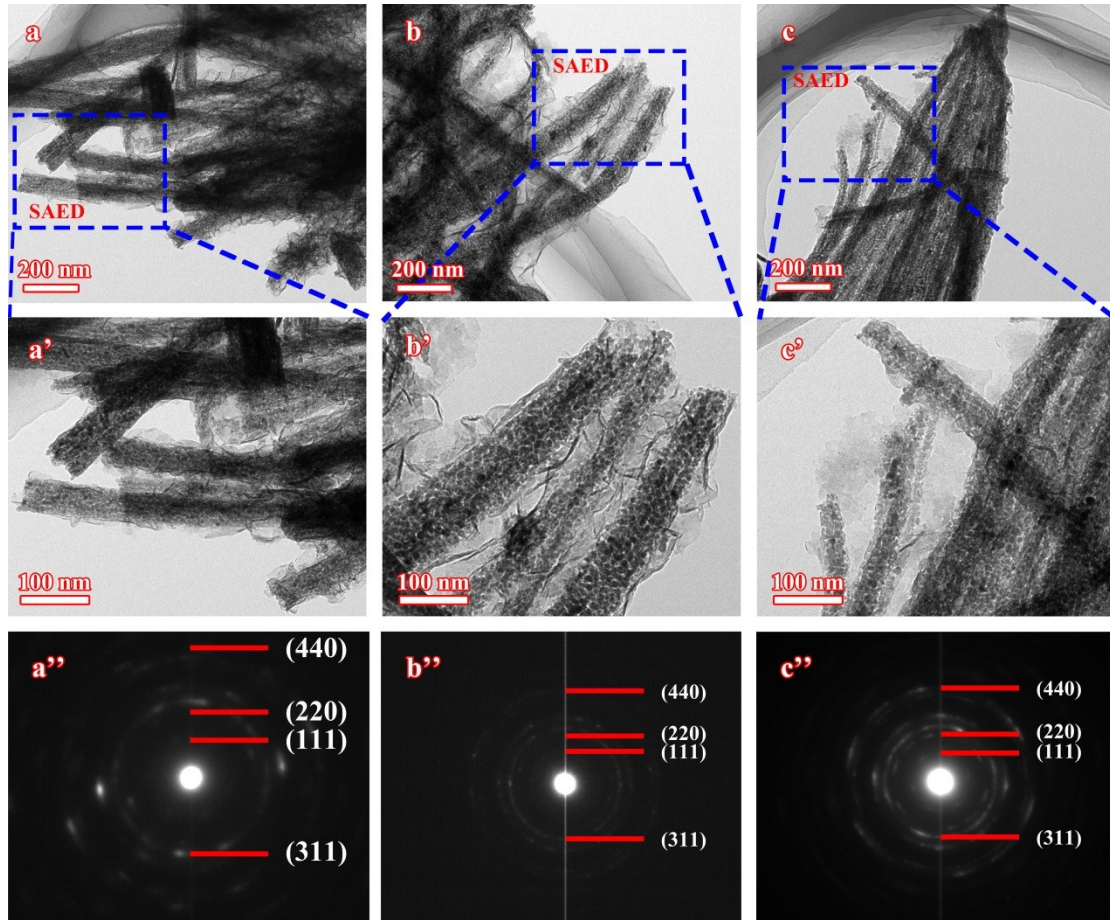
Fig. S6 The morphology of pristineNiCo$_2$O$_4$, H-NiCo$_2$O$_4$ 3 h and H-NiCo$_2$O$_4$ 4 h are shown in Fig. a, b, c respectively after 3000 cycles. The Fig. a', b', c' are the enlarged view of Fig. a, b, c respectively. The Fig. a'', b'', c'' are the SAED pattern of the pristine, H-3 h, H- 4h NiCo$_2$O$_4$ nanowires after 3000th cycle.