Synthesis of Free-Standing Spinel $FeCo_2S_4$ Nanoplates toward Improvement of Electrocatalytic Oxygen Evolution from Water Splitting

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Abstract

In this work, a system of $FeCo_2S_4$-catalyzed oxygen evolution reaction (OER) is studied. The spinel $FeCo_2S_4$ nanocatalyts are synthesized by a two-step hydrothermal method on a Ni foam (NF) by vulcanizing Fe-Co precursors with different [Na_2S], leading to the products of excavated nanospheres (ENSs). Besides, the structures of $FeCo_2S_4$ ENSs are stable after 12-hour OER durability test. Only the surface states of them are changed largely due to drastic leaching of sulfur. The phenomenon implies sulfur a key role on the surface instead of in the structure of an ENS for OER. In the results of potential-dependent XRD and XAS with the 0.1 M-$FeCo_2S_4$/NF electrode, the dominant pathway for $FeCo_2S_4$-catalyzed water splitting is via the formation of MOOH followed by release of O_2. Hence, the reason of S-assisted OER is due to optimization of conductivity to benefit the MOOH generation. This finding which was presented in few reports is now bringing a proof to confirm the absence of MSOH during the OER.

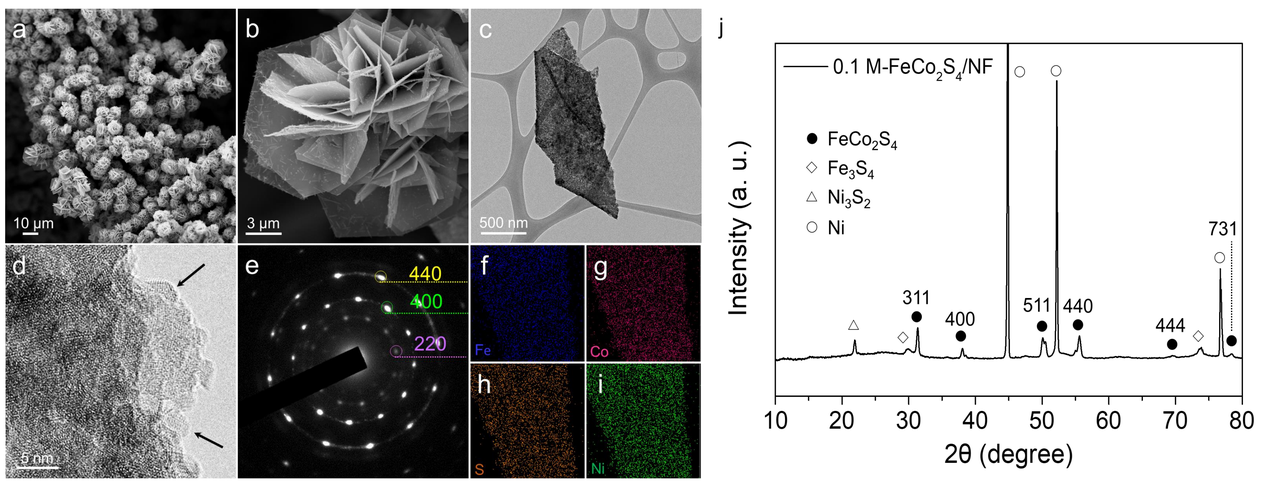

Figure 1. (a, b) SEM, (c, d) bright-field TEM images, (e) SAED, (f-i) STEM-EDS maps of $FeCo_2S_4$ excavated nanoballs, (j) its corresponding XRD pattern.

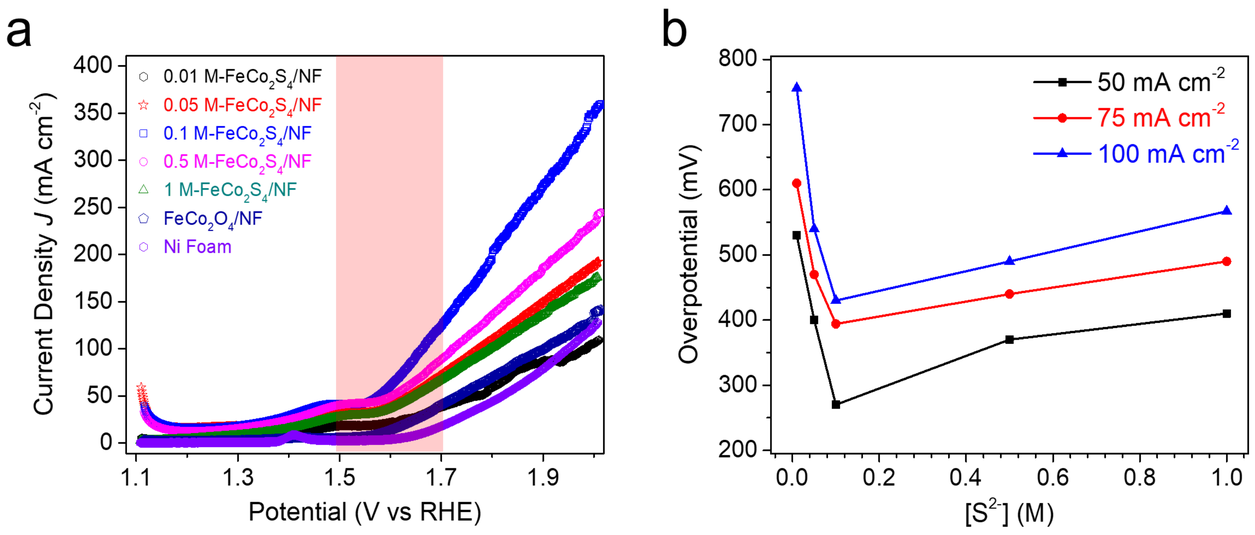

Figure 2. (a) OER backward LSV polarization curves, (b) plots of overpotential vs [S^{2-}] at 50, 75, 100 mA cm^{-2}.

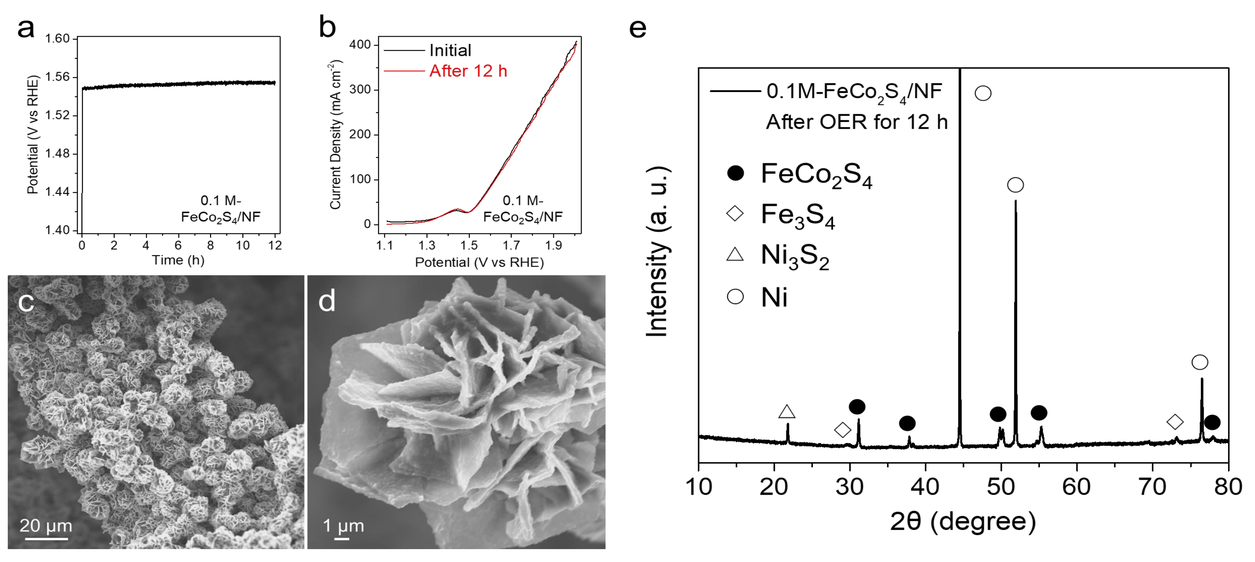

Figure 3. (a) Chronopotentiometry (CP) plot, (b) LSV curve, (c, d) SEM images, and (e) PXRD pattern of $FeCo_2S_4$ ENSs made with 0.1 M Na_2S after 12-hour durability test. The CP plot was obtained by running scan at a static current density of 50 mA cm^{-2} for 12 hours.

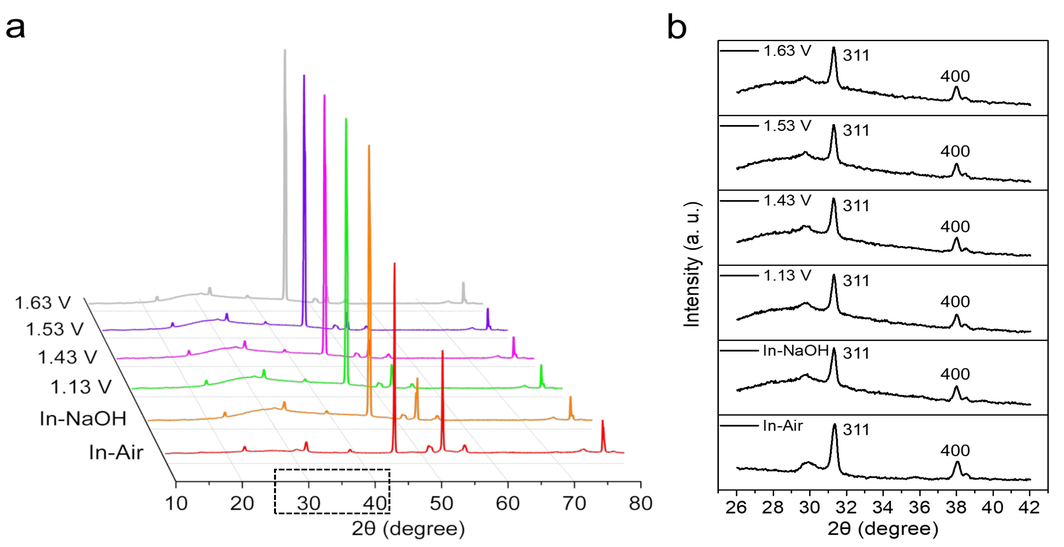

Figure 4. (a) Synchrotron XRD patterns of OER catalyzed with 0.1 M-$FeCo_2S_4$ ENSs at ambient (In-Air), in 1 M NaOH (In-NaOH), and selected potentials of 1.13 V, 1.43 V, 1.53 V, and 1.63 V. (b) The patterns within the selected 2-theta range where include the 311 and 400 peaks of spinel $FeCo_2S_4$.

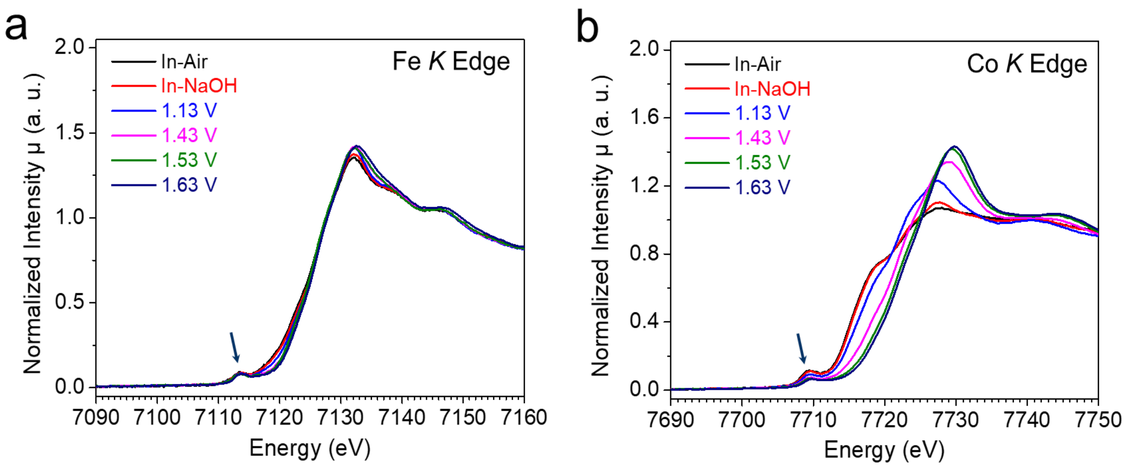

Figure 5. XANES of (a) Fe and (b) Co K edges for the 0.1 M-$FeCo_2S_4$/NF.

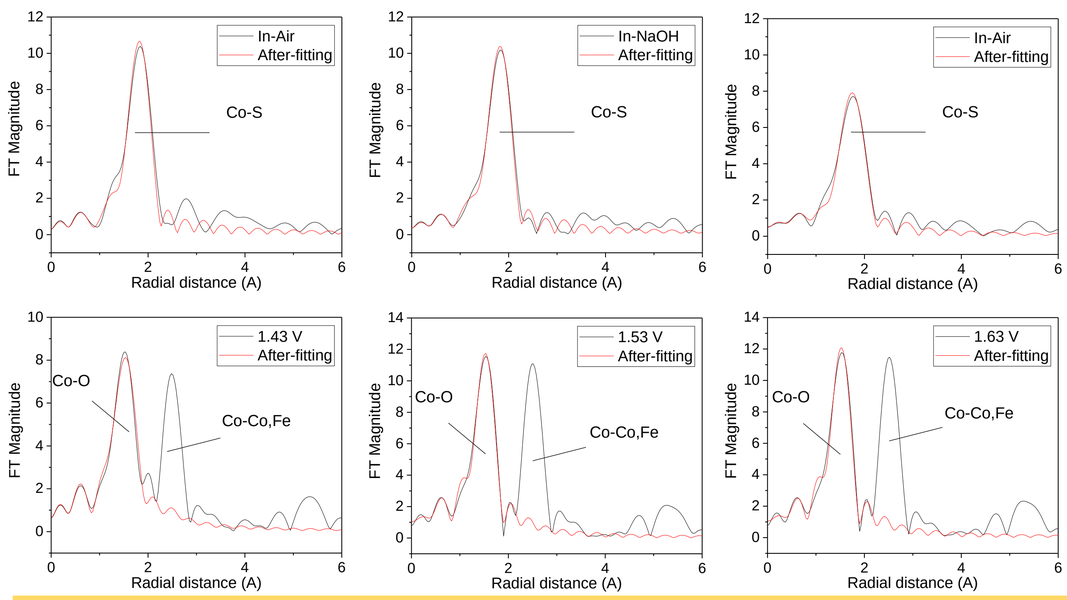

Figure 6. (a) Synchrotron EXAFS patterns of OER catalyzed with 0.1 M-$FeCo_2S_4$ ENSs at ambient (In-Air), (b) in 1 M NaOH (In-NaOH), and selected potentials of (c) 1.13 V, (d) 1.43 V, (e) 1.53 V, and (f) 1.63 V.

	N	$S0^2$	σ^2	R
In-Air	4	0.77	0.006	2.23
In-NaOH	4	0.77	0.006	2.23
1.13 V	4	0.77	0.008	2.21
1.43 V	5	0.754	0.008	1.9
1.53 V	6	0.667	0.005	1.9
1.63 V	6	0.667	0.005	1.9

Table 1. Fitting information of Co FT-EXAFS for 0.1 M-$FeCo_2S_4$/NF.

Reference

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