Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Support Information

Proposed electron transmission mechanism between Fe^{3+}/Co^{2+} and Fe^{3+}/Fe^{3+} in spinel structure and its practical evidence on quaternary $Fe_{0.5}Ni_{0.5}Co_2S_4$

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Table S1. The etching parameters of the two samples.

Sample	Etching element	Source Gun Tyoe	Total acquistition time	Number of Energy steps	Enegy step Size	Etching Time
$Fe_{0.5}Ni_{0.5}Co_2O_4$	Ar ion	Al Kα	1 min 8.0 secs	1361	1.00 eV	~3000 s
$Fe_{0.5}Ni_{0.5}Co_2S_4$	Ar iron	Al Kα	1 min 8.0 secs	1361	1.000 eV	~3000 s

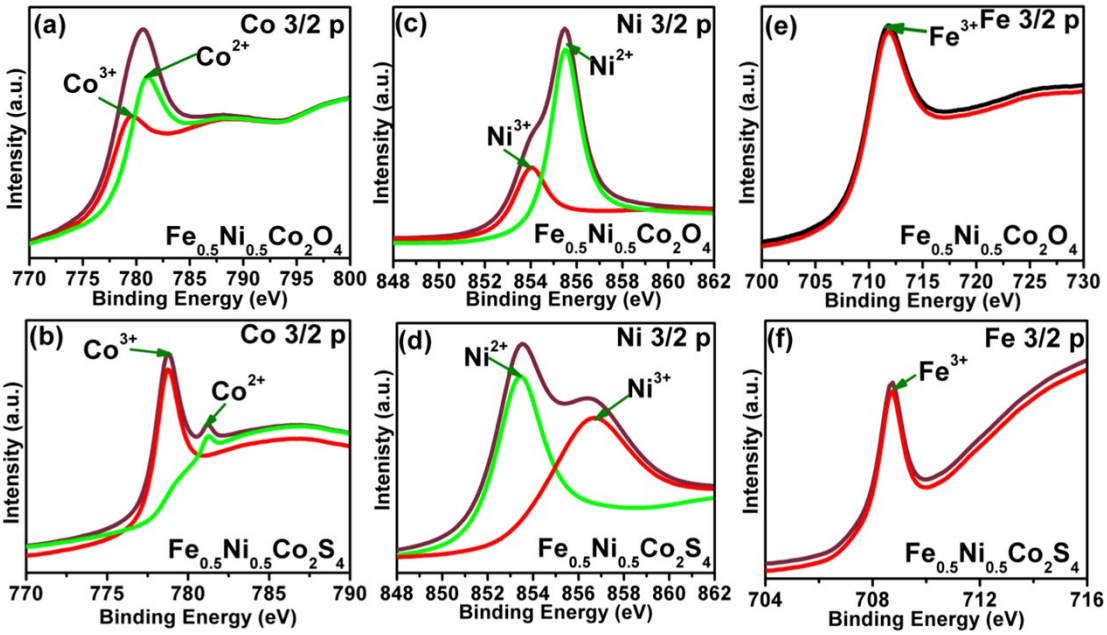

Figure S1. XPS data of $Fe_{0.5}Ni_{0.5}Co_2O_4$ and $Fe_{0.5}Ni_{0.5}Co_2S_4$ treated by Ar-cluster etching technique: (a, c, e): Co 3/2p, Ni 3/2p, Fe 3/2p of $Fe_{0.5}Ni_{0.5}Co_2O_4$; (b, d, f) Co3/2p, Ni 3/2p, Fe 3/2p of $Fe_{0.5}Ni_{0.5}Co_2S_4$.

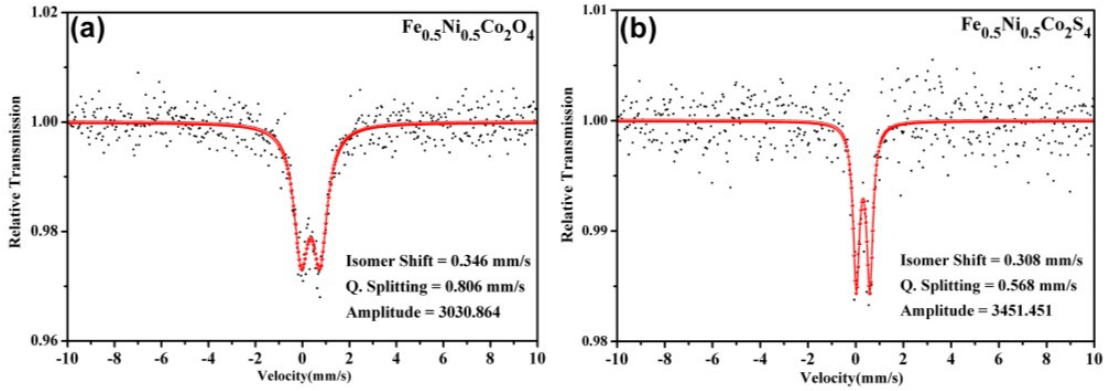

Figure S2. The Mössbauer of $Fe_{0.5}Ni_{0.5}Co_2O_4$ and $Fe_{0.5}Ni_{0.5}CoS_4$.

According to the Isomer shift value, we can get information that the Fe ions in both two samples presented tervalence. Besides, Fe^{3+} only can be found at B sites.[1-2]

[1] S.J. Kim, C.S.Kim; *Journal of the Korean Physical Society*, 2014, 64, 852-856.

[2] D. Polikarpov, V. Cherepanov, M. Chuev, R. Gabbasov, I. Mischenko, M. Nikitin,Y. Vereshagin, A. Yurenia,V. Panchenko. *Hyperfine Interace*, 2014, 226, 421–430.