Electronic Supplementary Information (ESI):

Self-assembled c-axis oriented antiperovskite soft-magnetic $CuNCo_3$ thin films by chemical solution deposition

Zhenzhen Hui,[a] Xianwu Tang,[a] Dingfu Shao,[a] Renhuai Wei,[a] Jie Yang,[a] Peng Tong,[a] Wenhai Song,[a] Xuebin Zhu[*a] and Yuping Sun[*abc]

*[*a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China. E-mail: xbzhu@issp.ac.cn*

*[*b] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China.*
E-mail: ypsun@issp.ac.cn

[c] Collaborative Innovation Centre of Advanced Microstructures, Nanjing University, Nanjing 210093, China.

Experimental Details

1. Raw materials decomposition and samples crystallization process

In order to give a clear image about the formation of $CuNCo_3$ phase, several experiments are carried out. After pyrolyzed, the thin films on Si(001) substrates were annealed at 800 ºC for 2h under air, then annealed at 800 ºC for 2h under the forming gas (20% H_2 and 80% N_2) and finally annealed at 800 ºC for 2h under flowing NH_3 atmosphere with 1 atm pressure.

Fig. 1S(a) shows the XRD θ-2θ pattern of the pyrolyzed thin film. During the pyrolysis process under air, cupric nitrate and cobalt acetate are decomposed and formed to metal oxide $Cu_{0.75}Co_{2.25}O_4$ (cubic, PDF Card no. 01-078-2176). Based on the reports about the metal acetate decomposition behavior, the organic residual would be decomposed to gas and water, and then evaporate in this process. Fig. 1S(b), (c) and (d) show the thin film annealed at 800 ºC for 2h under air, then annealed at 800 ºC for 2h under the forming gas (20% H_2 and 80% N_2) and finally annealed at 800 ºC for 2h under flowing NH_3 atmosphere, respectively. After annealed at 800 ºC for 2h under air, the phase is also of $Cu_{0.75}Co_{2.25}O_4$ with enhanced crystalline quality. Whereas, after annealed at 800 ºC for 2h under the forming gas (20% H_2 and 80% N_2), the $Cu_{0.75}Co_{2.25}O_4$ phase is reduced into metallic Cu element (cubic, PDF Card no. 01-085-1326) and Co element (cubic, PDF Card no. 01-089-7093). On the other hand, after annealed at 800 ºC for 2h under flowing NH_3 atmosphere, the metallic Cu and Co elements were transformed to the $CuCo_2N_{0.6}$ (cubic, PDF Card no. 00-053-0435) with some

residual Co element. It should be noted that the $CuNCo_3$ phase cannot form, which indicates that nitrogen atoms are difficult to incorporate into the cubic metal lattices. The chemical reaction mechanisms are as followings.

Pyrolysis processing:

$$Cu(NO_3)_3 + 3Co(CH_3COO)_2 + O_2 \xrightarrow{\text{Pyrolysis}(350^{\circ}C)} Cu_{0.75}Co_{2.25}O_4$$

Annealing under air:

$$Cu_{0.75}Co_{2.25}O_4 \xrightarrow{\text{Air}(800^{\circ}C)} Cu_{0.75}Co_{2.25}O_4(\text{enhanced crystallize quality})$$

Annealing under the forming gas (20% H_2 and 80% N_2)

$$Cu_{0.75}Co_{2.25}O_4 + H_2 \xrightarrow{800^{\circ}C} Cu + Co$$

Annealing under NH_3 atmosphere

$$Cu + Co + NH_3 \xrightarrow{800^{\circ}C} CuCo_2N_{0.6} + Co$$

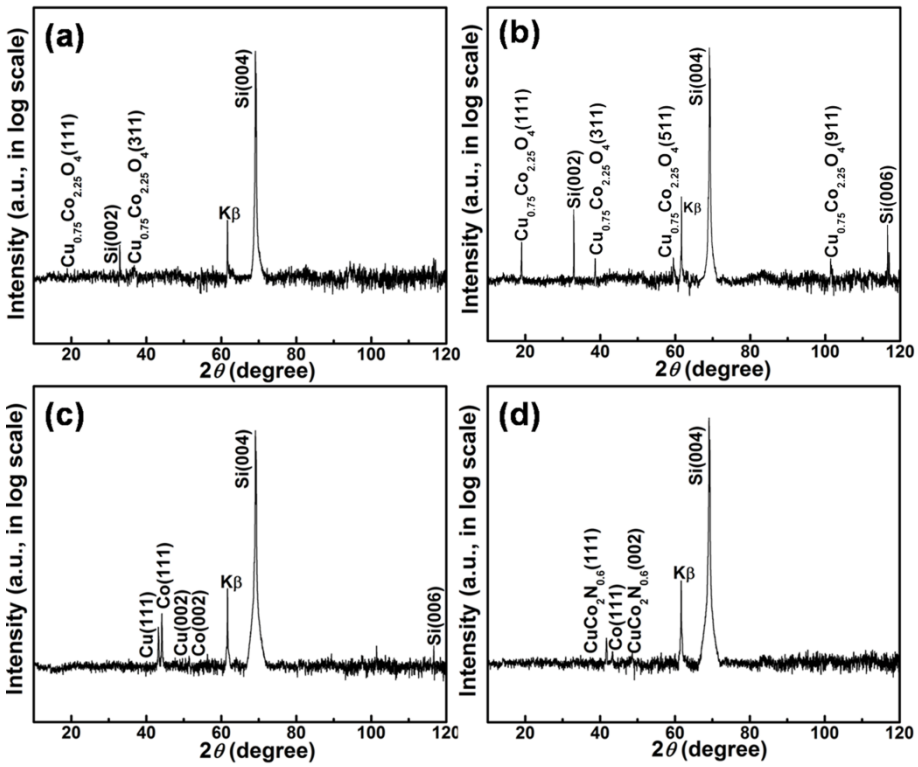

Fig. 1S XRD patterns for (a) the pyrolyzed thin film (b) the thin film annealed at 800 ºC for 2h under air and (c) the thin film annealed at 800 ºC for 2h under the forming gas (20% H_2 and 80% N_2) and (c) the thin film annealed at 800 ºC for 2h under NH_3 atmosphere deposited on Si(001) substrates.

2. Theoretically calculations

In order to verify the metallic ground state of $CuNCo_3$, the density functional theory (DFT) calculations are performed. Fig. 2S(a) shows the spin polarized density of states (DOS) near Fermi energy (E_F) of $CuNCo_3$. One may notice the DOS near E_F is predominately contributed by the 3*d* electrons of Co. No band gap was observed. On the other hand, since Co is the transition metal atom with unfulfilled 3*d* electrons, the correlation of 3*d* electrons might influence the electronic structure. Thus we also calculated the DOS under different Hubbard U. As shown in Fig. 2S(b), Hubbard U influences the shape of DOS. However, even the very large U of 5 eV cannot open a band gap. Therefore, based on the DFT calculations, the metallic ground state of $CuNCo_3$ is very robust and our observation is reliable.

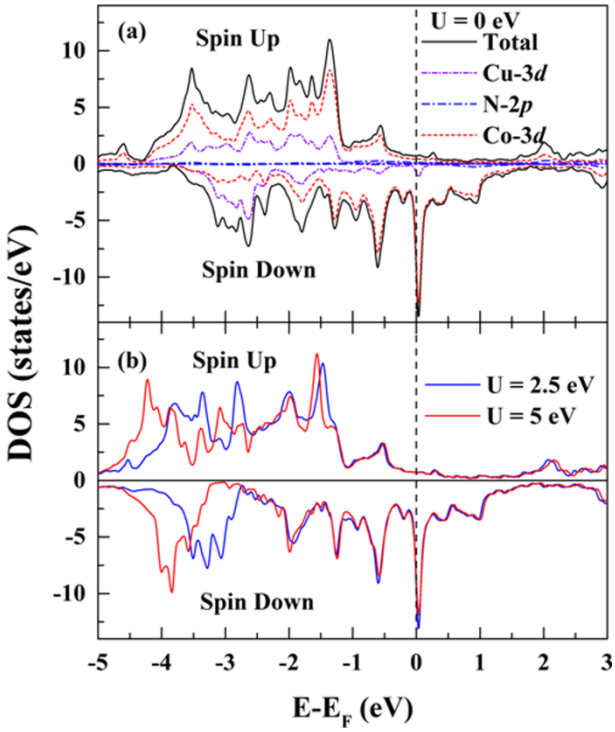

Fig. 2S(a) DOS of $CuNCo_3$ for U = 0 eV, (b) DOS of $CuNCo_3$ for U = 2.5 and 5 eV.