

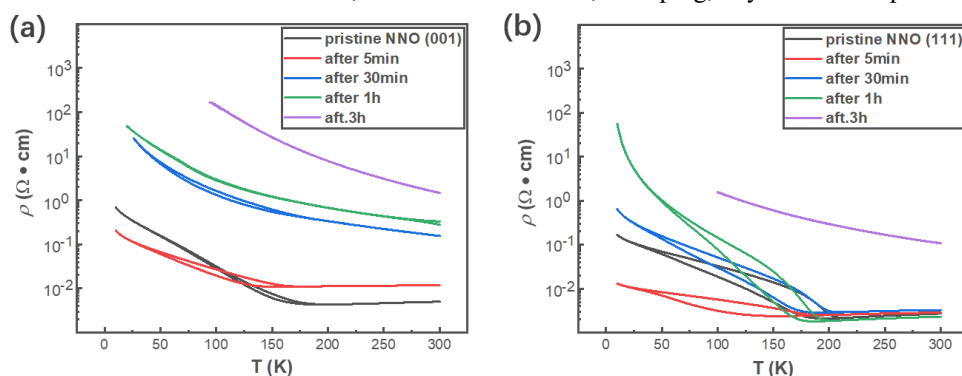
## Hydrogenation Induced Phase Transition Modulation in Perovskite Nickelates Assisted by Metal-Acid System

SANKEN, Osaka Univ.<sup>1</sup>, NSRL, USTC<sup>2</sup> Hui Ren<sup>1</sup>, Ai I. Osaka<sup>1</sup>, Azusa N. Hattori<sup>1</sup>,  
Boyuan Yu<sup>1</sup>, Chongwen Zou<sup>2\*</sup>, Hidekazu Tanaka<sup>1\*</sup>

Email: renhui77@sanken.osaka-u.ac.jp

Perovskite rare earth nickelates ( $\text{RNiO}_3$ ,  $\text{R}=\text{Pr}, \text{Nd}, \dots$ ) display excellent metal-insulator transition (MIT) properties which are promising for the applications in novel electronic devices. As one of the typical perovskite oxides in  $\text{RNiO}_3$  family,  $\text{NdNiO}_3$  (NNO) with sharp MIT isothermally induced by chemical doping of hydrogen has attracted tremendous attention. Recently, hydrogenation in transition metal oxides<sup>1,2</sup> based on metal-acid system was validated by experiments and calculations. Compared with traditional high temperature catalytic strategy, it is more easier to achieve hydrogenation that does not require extreme condition such as high temperature, noble-metal catalyst. In this work, we first successfully achieve a tunable phase modulation in NNO film on STO (001) and STO (111) substrates in acid (1wt%  $\text{H}_2\text{SO}_4$ ) solution, which by the attachment of metal (Zn) particle on the surface of NNO. Figure (a) and (b) show the resistivity-temperature ( $\rho$ - $T$ ) curves for NNO/STO film against immersion time in acid. With increasing immersion time, the resistivity of NNO (001) systematically increased and metallic phase disappeared at room temperature in Fig. (a). The mechanism could be explained based on an electron-proton co-doping, which is consistent with our experiment results obtained in the In-situ X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectrum (SIMS). Furthermore, we find that there is an interesting facet dependence during hydrogen doping (H-doping) by metal-acid method, namely NNO film on STO (111) exhibited slower change in hydrogenation induced insulating phase, and rather stabilized metal behavior at room temperature in the initial metal-acid treatment (within 1h), which is shown in Fig. (b), indicating the possible existence of energetically favored pathway for hydrogen diffusion along the direction of [001] in NNO film. Our current findings will supply opportunities for the development of tunable H-doping in other perovskite oxides of  $\text{RNiO}_3$  family at ambient condition without additional high-energy consumption.

**Keywords:** Metal-insulator transition, Rare-earth nickelates, H-doping, Crystal facet-dependence



**Fig.1** The MIT modulation with facet dependence during hydrogenation assisted by metal-acid system. (a) The hydrogenation induced insulator behavior of NNO (001) was observed at room temperature after treatment 1h. However, (b) there is still remain metal behavior of NNO (111) at room temperature after the same treatment time.

### References

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