In-situ Metallic Nanoparticles Exsolution on Perovskite Parent Driven by Crystal Reconstruction

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Abstract: Metallic nanoparticles (NPs) supported functional perovskite catalysts require high-density particles with even distribution and reliable thermal stability. Herein, we report an interesting phenomenon that the creation of layered oxygen deficiency triggered by *in-situ* crystal reconstruction of double perovskite can spontaneously lead to fast exsolution of B-site cations to segregate massively and uniformly dispersed NPs with high stability. DFT calculation verifies that the crystal reconstruction induced coordinated oxygen loss is the driving force of fast B-site segregation. The prepared material shows promising potential as an active electrode for solid oxide fuel cell (SOFC) and electrolysis cell (SOEC) for CO_2 reduction.

Keywords: Crystal reconstruction; Double perovskite; *in-situ* exsolution.

1. Introduction

Tremendous endeavor has been devoted to synthesizing highly active supported NPs catalysts for energy conversion and storage devices. Specifically, planting NPs has been proven to be a promising approach to enhance both the catalytic activity and durability of the state-of-the-art perovskite catalysts for SOFCs[1] and SOECs applications[2]. Unlike traditional impregnation method, the exsolution process provides a promising pathway to design and synthesize NPs with better thermal stability and dispersion, which can usually drive B-site cations moving out their parent lattice. In fact, for the whole perovskite family, the information has not been available in terms of either the experimental data from *in-situ* visual observations of the NP exsolution process or systematical and theoretical calculations to support a given assumption explaining the nature of exsolution triggering force[3].

In this work, we discovered that *in-situ* crystal reconstruction was determined as the driving force steering the fast growth of uniformly dispersed metallic stable NPs on Co-doped $Pr_{0.5}Ba_{0.5}MnO_x$ (PBMCo) layered double perovskite. The crystal reconstruction in a reducing atmosphere induced the formation of layered structure and creation of ordered massive oxygen vacancies, further decreasing the oxygen coordinating number of the Co ion as well as the energy required to drag out the B-site cations. In addition, we utilized atomic-scale *in-situ* characterization technologies to have directly visualized this fast NP exsolution process, which provided a deeper and more thorough understanding of this phenomenal process.

2. Experimental

The 10 mol% of Co doped $Pr_{0.5}Ba_{0.5}MnO_3$ were prepared by a modified sol-gel method. Certain amount of Pr, Ba, Mn and Co nitrate salts were dissolved in distilled water with the addition of quantitative amounts of citric acid and ethylene glycol. The solution was continuously stirred on a hotplate at 60 °C until the gel formed. The gel was slowly decomposed at 350 °C for 2h and calcined in air at 950 °C for 4h. The prepared materials were denoted as PBMCo. In the meanwhile, the samples after TGA analysis at 500 °C, 850 °C, and 850 °C for 4h test were denoted as PBMCo-500, PBMCo-850, PBMCo-850-4h, respectively.

3. Results and discussion

The multi-step weight loss of PBMCo associated with the high temperature reduction treatment was initially deduced by TGA, as shown in Figure 1(a). From the structure standpoint, the formula of the material was changed from $Pr_{0.5}Ba_{0.5}Mn_{0.9}Co_{0.1}O_3$ to a layered $PrBaMn_{1.8}Co_{0.2}O_5$ with the treatment in a reducing atmosphere during this period[3]. The A-site in one single unit cell was doubled, and Mn or Co was sandwiched between the PrO_x and BaO layers with the formula: ([BaO]-[Mn/CoO_x]-[PrO_x]- [Mn/CoO_x]-[BaO]). Simultaneously, oxygen in the PrO_x plane was removed, further creating more oxygen vacancies and the two dimensional oxygen diffusion channels, which could be responsible for the initial weight loss of 5.5 wt%. By comparing the reducibility of all elements in PBMCo, it can be speculated that the main weight loss should be related to the reduction of ionic Co to metallic Co combined with the loss of oxygen bonding with Co. In stage 4, any further increase of the reduction time did not lead to obvious weight losses, indicating that no reduction reactions occurred in this stage.

It was infered that the reduced bonding energy for stabilizing Co in the lattice, as well as the channel for diffusing lattice oxygen ions, should be responsible for the exsolution of metallic Co. To verify our prediction, the exsolution process was simulated, and the energy consumed was calculated based on the DFT using the Vienna ab initio simulations package (VASP) code. The calculated defect formation energies of $PrBaMn_{1-x}\square O_5$ ($AA'BB'O_5$) with the appearance of one Co atom was calculated to be -3.62 eV. In comparison, that of $PrBaMn_{1-x}Co_xO_6$ ($AA'BB'O_6$) was estimated to be -4.82 eV. Consequently, it can be concluded that the formation of a layered structure was much favorable for the exsolution of B-site Co.

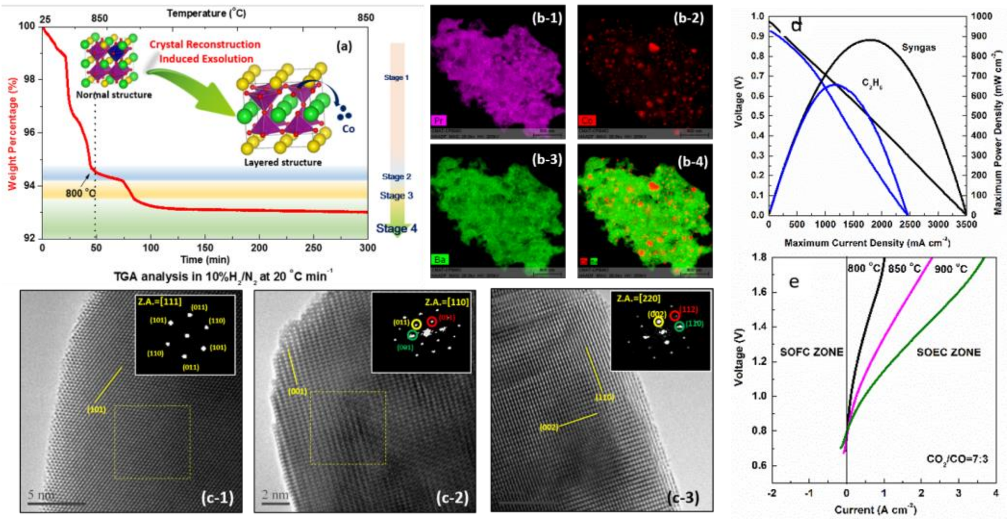

Figure 1. (a) Thermogravimetric analysis of PBMCo in 10% H_2-N_2. (b) HAADF image of the PBMCo-850-4 h materials overlaid with the EDX elemental map of Pr, Ba and highlighted Co nanoparticles. (c) High resolution transmission electron microscopy (HR-TEM) images of fresh PBMCo (c-1), PBMCo-500 (c-2), and PBMCo-850-4 h (c-3). The diffractograms and their simulations are shown as insets in the images. The regions where the diffractograms were obtained are marked by yellow squares. (d-e) Electrochemical properties of PBMCo in SOFCs and SOECs: (d) Current–voltage curves and the corresponding power densities of the PBMCo anode in various fuels. (e) Temperature dependent I-V curves for CO_2 electrolysis with a feed composition of CO_2/CO=7/3 at increasing temperatures (800 to 900 °C).

4. Conclusions

In summary, the crystal reconstruction of PBMCo to a layered double structure induced the formation of a high concentration of O-vacancies and numerous *in-situ* exsolved nano Co particles with uniform dispersion. This fast exsolution process was, for the first time, observed and monitored by environmental TEM technologies. The results of the DFT calculation indicated a much lower formation energy for metallic Co from the layered perovskite structure. The fabricated material demonstrated outstanding performance and superior stability in SOFC mode fed with various fuels and in SOEC mode for CO_2 electrolysis. Thus, it represents a promising approach to prepare thermally stable NPs supported on other functional catalysts.

References

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