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Ion Beam as an External and Dynamic Metal Reservoir to Induce Nanoparticle Exsolution in Oxides

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Nanoparticle exsolution is a recently developed method to produce oxide-supported metal nanoparticles via phase precipitation. It has attracted significant attention in the field of solid oxide fuel cells and electrolyzers (SOFC/SOEC) due to its potential for producing active and nanostructured electrodes. However, conventional exsolution methods face challenges in reaching the solubility limit of metal ions in the oxide matrix. To overcome this issue, here we propose a new approach to induce exsolution by using ion beams as an external and dynamic metal reservoir. We demonstrate the effectiveness of this method by using thin-film $Zr_{0.5}Ce_{0.5}O_2$ (CZO) as a model system. Through ion irradiation experiments, 10 keV Ni ions were implanted into the near-surface regions of CZO films, and then exsolved as nanoparticles on the surface. This research offers a promising new avenue for developing next-generation SOFC/SOEC electrode materials using irradiation-tailored exsolution.

Introduction

The creation of nanocatalysts (1, 2) that are stable, efficient, and cost-effective is essential for various electrochemical applications such as solid oxide fuel/electrolysis cells (SOFC/SOEC) (3, 4) and chemical membrane reactors (5). A promising new technique for generating metal nanoparticles for these applications is called "exsolution" (6, 7), which involves a phase precipitation process. Initially, metal cations are dissolved in the host oxide to create solid solutions, after which they are precipitated out of the oxide via a single-step (electro)chemical reduction (8-12) as well-dispersed metal nanocatalysts. These exsolved nanoparticles are anchored in the host oxide (13-16), making them more stable than those produced through physical deposition or wet impregnation techniques (9, 17). Furthermore, exsolved nanoparticles can dissolve and regenerate during redox cycling (9, 18, 19), which enhances their lifespan as catalysts. Given these desirable properties, exsolution has become a powerful nano-structuring tool in fabricating energy materials.

However, traditional exsolution techniques involve dissolving the metal cations in the host oxide at the start, which limits the materials that can undergo exsolution (both the exsolved metal and host oxides) due to solubility constraints (20, 21). Thus, there is a pressing need to develop approaches that can broaden the range of materials eligible for exsolution.

Here, we present a new approach to induce nanoparticle exsolution in oxides using metal ion irradiation. The central idea is to use implanted metal ions (22, 23) as an external source of metal for exsolution. To demonstrate this method, we examined the exsolution behavior of epitaxial $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (CZO) films when subjected to 10 keV Ni irradiation. CZO is a widely used catalyst in many catalytic reactions (24-26). However, because of the low solubility of transition metal cations in CeO_2 -based materials (27, 28), it is challenging to achieve a uniform metal- CeO_2 solid solution using conventional exsolution synthesis. Our findings show that Ni irradiation can effectively decorate the CZO surfaces with well-dispersed nanoparticles, indicating that metal ion beams can be used as an external metal source to initiate exsolution. The primary advantage of this approach (referred to as irradiation-tailored exsolution) is that metal ions do not need to be dissolved in host oxides beforehand, overcoming the solubility issue that conventional exsolution methods face.

Experiment

Film Deposition. $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (CZO) films with a thickness of 30 nm were deposited through Pulsed Laser Deposition (PLD) using a KrF excimer laser with a wavelength of 248 nm. (001)- and (111)-oriented yttria-stabilized zirconia (YSZ) single crystal substrates with dimensions of 10 mm \times 5 mm \times 0.5 mm (supplied by MTI Corporation with one-side polished surface) were utilized. The backside substrate temperature was maintained at 750 °C with an oxygen pressure of 20 mTorr throughout the deposition process.

Film Characterization. The Cypher S AFM Microscope was employed to gather atomic force microscopy (AFM) images utilizing tapping mode. The AFM tips that were utilized were the AC160TS-R3 type from Oxford Instruments. To circumvent any edge effects, the center of the sample was characterized by AFM. X-ray diffractions (XRD) were conducted utilizing Cu K-alpha 1 radiation with a Rigaku SmartLab X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Physical Electronics Versaprobe II X-ray Photoelectron Spectrometer with a monochromatic Al K α source.

Ion beam irradiation. At the Cambridge Laboratory for Accelerator-based Surface Science (CLASS), Tandem accelerator was utilized to generate 10 keV Ni beams. For each irradiation experiment, the main chamber was pumped down to 10^{-6} Torr at room temperature, followed by heating the sample to 800 °C with a ramp rate of approximately 200 °C per minute. The incident ion beam was parallel to the surface normal. An aperture size of 8 mm in diameter, which is comparable to the sample geometry, was used to achieve a uniform irradiation dose distribution throughout the surface. Throughout the experiments, the pressure of the main chamber was actively maintained to be around 10^{-5} Torr. After irradiation, the sample was cooled naturally in the same environment to 100 °C before being removed from the chamber. The Ni dose of each sample was controlled to be 10^{15} cm $^{-2}$.

Stopping and Range of Ions in Matter (SRIM) simulation. The SRIM-2013 software (29) was used in this study to simulate ion-matter interactions between the Ni beam and

CZO. To conduct the simulation, we used a similar composition, CeO_2 , instead of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (CZO), as CeO_2 has well-established threshold displacement energies that are critical input parameters in the SRIM simulation. The simulation involved 10 keV Ni ions bombarding stoichiometric CeO_2 at normal incidence, consistent with the experimental setup. A total of 10^6 ions were simulated using the “monolayer collision step/surface sputtering” option. For Ce and O, the threshold displacement energies (E_d) were set to 56 and 27 eV, respectively, based on previous atomistic simulations (30).

Results and Discussion

Figure 1a depicts the experimental configuration used for the ion irradiation experiments. Two types of CZO films were subjected to examination: (001)- and (111)-oriented CZO films. The crystalline orientations of these films were determined through out-of-plane X-ray diffraction (XRD), and the corresponding XRD patterns are presented in Figure 1b and Figure 1c. It can be observed that both types of CZO films are single crystalline and exhibit the intended lattice orientations.

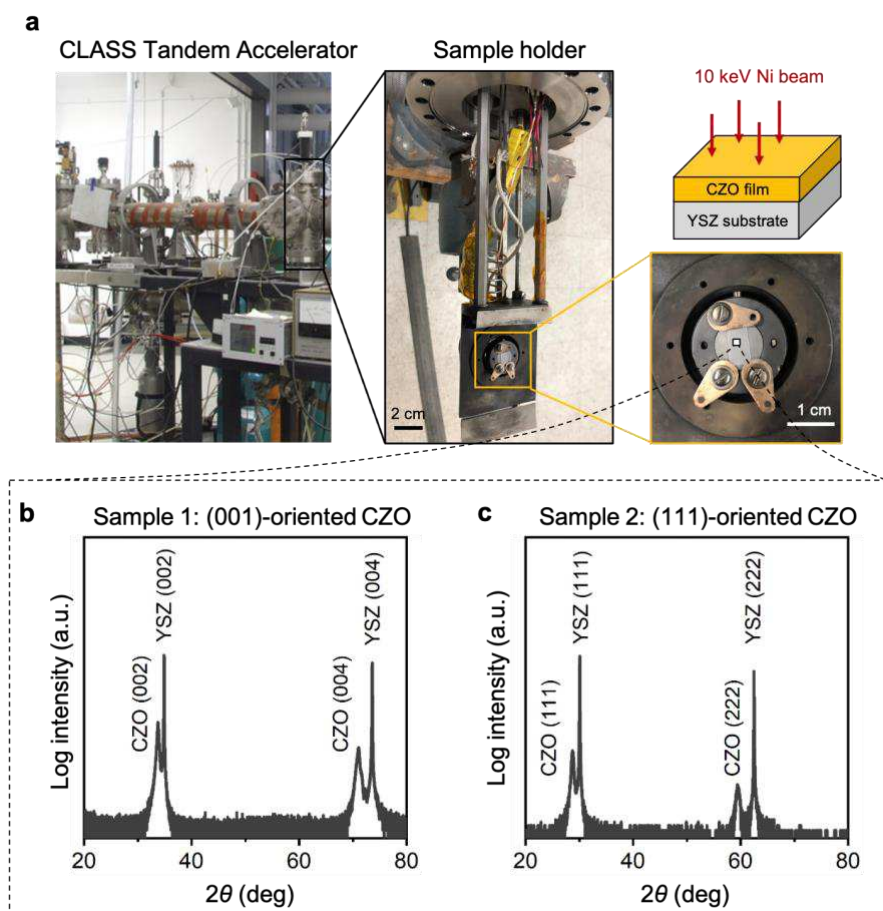


Figure 1. Experimental setup and sample characterization. (a) 10 keV Ni ion beams are generated from a Tandem accelerator for the irradiation experiment. (b-c) Out-of-plane X-ray diffraction showing two types of CZO films used in this study: (001)- and (111)-oriented CZO epitaxial films grown on single-crystalline YSZ substrates.

During the experiment, we subjected the CZO films to a 10 keV Ni ion beam at normal incidence. To clarify the interactions between the 10 keV Ni ion beam and the CZO film, we conducted SRIM simulation and presented the findings in Figure 2. The results indicate that a majority of the Ni ions were implanted in the near-surface region (top 20 nm) of the CZO films.

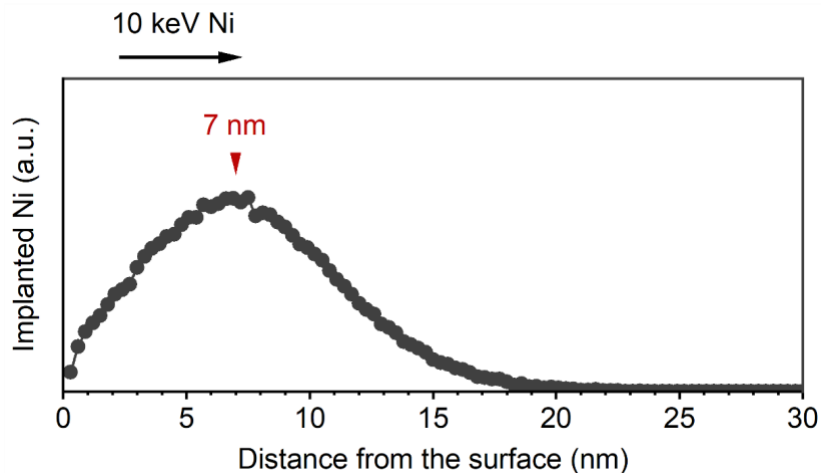


Figure 2. SRIM simulation of the Ni concentration profile in CeO₂ from 10 keV Ni irradiation at normal incidence. It is important to note that the CeO₂ surface is implanted with 10 keV Ni ions up to a depth of 20 nm.

Figure 3 summarizes the changes in surface morphology of (001)- and (111)-oriented CZO films caused by irradiation. The figures show that both types of CZO films have a smooth surface in their as-prepared state. However, after irradiation, nanoparticles are visibly present on the surface of both types of CZO films. This suggests that Ni irradiation can effectively generate nanoparticles on CZO films, irrespective of their lattice orientation.

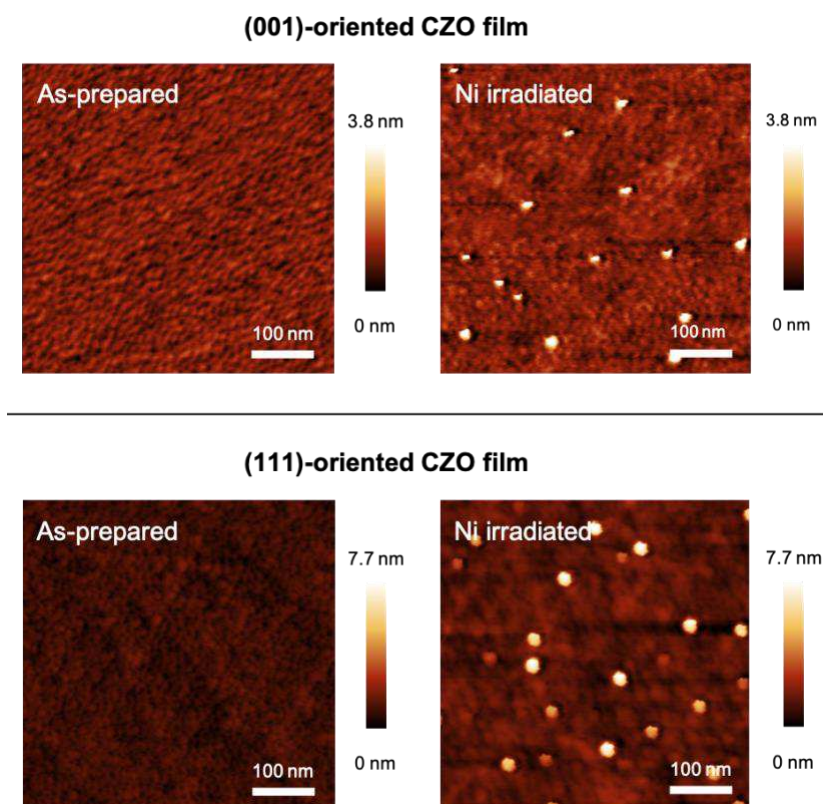


Figure 3. Surface morphologies of the (001)- and (111)-oriented CZO films before and after Ni ion irradiation, probed by AFM. Note that surface nanoparticles can be clearly visualized on the surface of both types of CZO films after Ni irradiation.

To further clarify the chemical composition of the surface nanoparticles, we conducted *ex-situ* XPS measurements on another (111)-oriented CZO film in two states: as-prepared and immediately after Ni irradiation. As depicted in Figure 4, the as-prepared CZO surface displayed no evidence of Ni species, which is consistent with our expectations. However, following Ni irradiation, Ni signals were detected in the XPS spectra (Figure 4b), alongside the emergence of surface nanoparticles (Figure 4a). This correlation suggests that the surface nanoparticles are indeed Ni nanoparticles. Thus, our findings confirm our hypothesis that ion beams can serve as an external metal source to trigger metal nanoparticle exsolution in oxides.

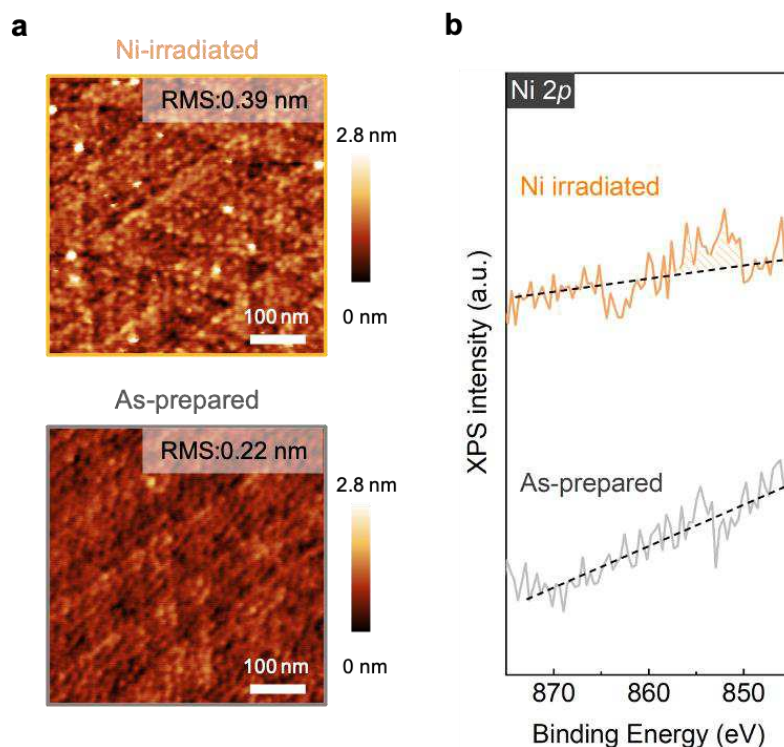


Figure 4. Surface chemical analysis of CZO films. (a) AFM images and (b) XPS spectra of the (111)-oriented CZO films in the as-prepared state and after Ni irradiation. Note that surface Ni species appeared in the XPS spectra after Ni irradiation, together with formation of surface nanoparticles. These findings suggest the observed surface nanoparticles in AFM images are Ni.

Conclusion

Using (001)- and (111)-oriented thin-film $\text{Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$ (CZO) as model systems, we successfully demonstrated that metal ion beams can function as an external metal source to prompt metal exsolution in oxides. We discovered that, following 10 keV Ni irradiation, the implanted Ni ions were effectively exsolved as nanoparticles on the CZO surface. Furthermore, we found that this approach is not limited to specific crystalline orientations of CZO. Given that ion irradiation is an external stimulus, this method can help address the solubility limit challenge of host oxides in conventional exsolution methods, allowing for a wider range of oxide materials to be applied in exsolution. We anticipate that this advancement will pave the way for producing next-generation SOFC/SOEC electrode materials through well-controlled metal nanoparticle exsolution.

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