

## Formation mechanism of high-entropy alloy nanoparticles assisted by hydrogen spillover effect

High-entropy alloys (HEAs) have recently received significant attention in various research fields. These alloys represent a new class of metallic materials in which more than five near-equimolar components are mixed to form single-phase solid solutions with high mixing entropy values, rather than intermetallic phases. Various unique synergistic effects result from such mixtures, including high configuration entropy, lattice distortion, sluggish diffusion and cocktail effects, and endow HEAs with high mechanical strength, good thermal stability and superior corrosion resistance. However, the development of HEA nanoparticles (NPs) with a mean diameter of less than 10 nm lags significantly behind, despite the potential practical applications of these NPs in catalysis, nanoelectronics and material science.

Hydrogen spillover is a fascinating phenomenon that occurs in sensors, hydrogen storage materials and heterogeneous catalysis. In this process, dissociated H atoms migrate to adjacent hydrogen-poor metal oxide surfaces via coupled proton/electron transfer. We demonstrate that titanium dioxide (TiO<sub>2</sub>) is a promising platform for the low-temperature synthesis of supported CoNiCuRuPd HEA NPs driven

by the pronounced hydrogen spillover effect on TiO<sub>2</sub>. This study also revealed the specific mechanism responsible for the formation of HEA NPs, on the basis of *in situ* characterization techniques.

CoNiCuRuPd HEA NPs supported on TiO<sub>2</sub> (CoNiCuRuPd/TiO<sub>2</sub>) were synthesized by a simple impregnation method, employing an aqueous solution of the corresponding precursors. This was followed by reduction under a H<sub>2</sub> atmosphere at 400°C. *In situ* X-ray absorption fine structure (XAFS) analyses were acquired at SPring-8 BL01B1 in conjunction with a Si (111) monochromator under a H<sub>2</sub> atmosphere at elevated temperatures (Fig. 1). X-ray absorption near-edge structure (XANES) spectra confirmed the reduction of all the precursors at 200°C. The intermediate shapes and edge positions at the Co and Ni K-edges indicated the presence of a mixture of cations and zero-valent ions at 200°C, because of their relatively low reduction potentials. In contrast, all spectra acquired at 400°C resembled those of the corresponding foils, suggesting that all the elements were in a metallic state.

Fourier transforms of extended X-ray absorption fine structure (FT-EXAFS) data further clarified

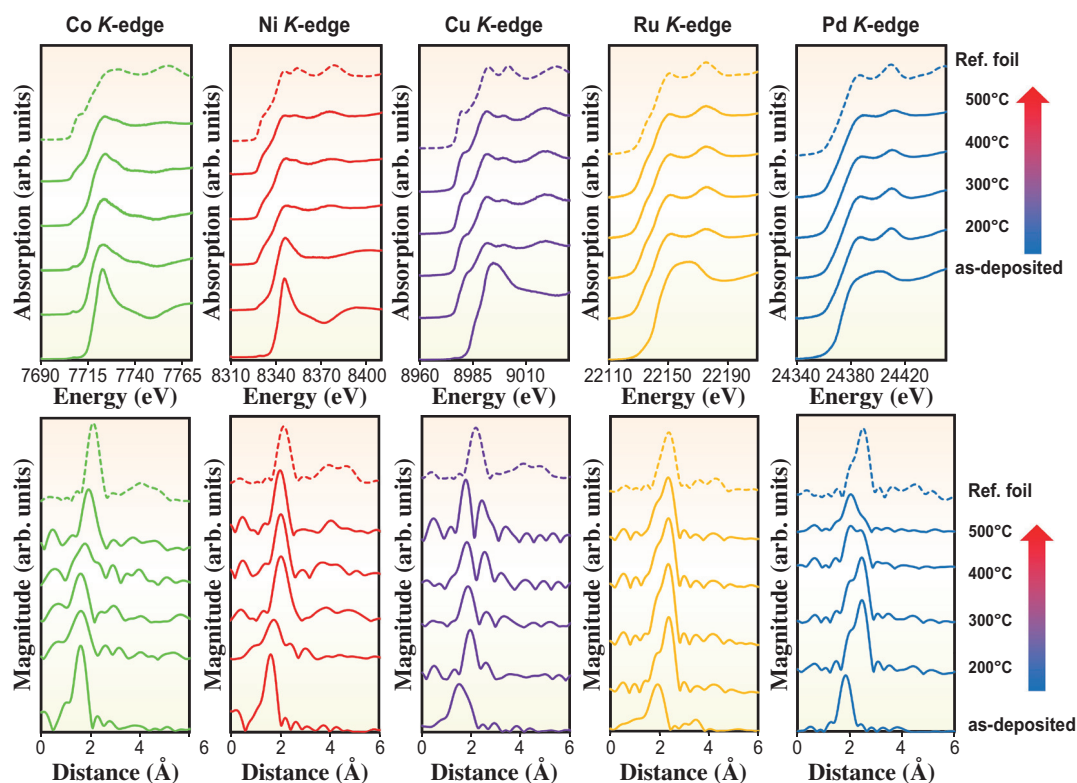


Fig. 1. *In situ* XANES and FT-EXAFS spectra at the Co, Ni, Cu, Ru, and Pd K-edges of CoNiCuRuPd/TiO<sub>2</sub> acquired during reduction in H<sub>2</sub> from room temperature to 500°C, and the corresponding reference foil materials (dotted line).

the structural transformation during the reduction sequence. The spectra of the as-deposited sample produced a sharp singlet peak in the *K*-edge region that was attributed to M–O bonds with lengths of approximately 1.7–1.9 Å. In the case of Co and Ni, the peak intensity due to the M–O bonds decreased at 200°C, whereas another peak attributed to metallic M–M bonds with longer interatomic distances appeared for Cu, Ru and Pd. These transitions demonstrated the reduction of M<sup>n+</sup> ions on the TiO<sub>2</sub> support. The bond structure after the completion of the reduction revealed that the interatomic metallic M–M bond lengths were significantly different from those for the corresponding bulk references. In the case of the Ru *K*-edge, the shouldered peak was observed at around 1.9 Å, which is suggestive of the formation of Ru–M with shorter interatomic distances. These results suggest that all elements were surrounded by different metallic atoms.

Considering *in situ* XAFS results as well as the result of other characterization methods, such as STEM and H<sub>2</sub>-TPR, we propose a mechanism for the formation of the HEA NPs on the TiO<sub>2</sub> support in conjunction with hydrogen spillover (Fig. 2). In a H<sub>2</sub> atmosphere, the Pd<sup>2+</sup> precursors are first partially reduced to generate nuclei. Following this, H<sub>2</sub> is dissociated on the surfaces of these Pd nuclei to form Pd–H species (Step 1). The reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> together with the transfer of H atoms from Pd nuclei at the metal-support interfaces (Step 2) is accompanied by the migration of electrons from Ti<sup>3+</sup> ions to neighboring Ti<sup>4+</sup> ions. This promotes the subsequent simultaneous transfer of protons to O<sup>2-</sup> anions attached to these adjacent Ti<sup>4+</sup> ions (Step 3). In this manner, the hydrogen atoms rapidly reach all metal ions by moving over the TiO<sub>2</sub> surface (Step 4), such that these ions are all reduced at the same time to form the HEA NPs (Step 5) accompanied by the regeneration of Ti<sup>4+</sup>. The *in situ* XRD pattern of CoNiCuRuPd/TiO<sub>2</sub> after reduction in H<sub>2</sub> at 200°C, which was conducted at BL01B1, showed the broad peak due to Pd (111). This peak disappeared with increasing reduction temperature, accompanied by the appearance of new peaks due to the formation of HEA NPs. *In situ* FT-EXAFS spectra at the Pd *K*-edge of CoNiCuRuPd/TiO<sub>2</sub> acquired in H<sub>2</sub> at 200°C showed a strong peak due to the contiguous Pd–Pd bond, which slightly shifted toward a shorter interatomic distance with increasing temperature. These are clear evidence of the formation of Pd nuclei in the early stage, which act as uptake sites to enhance the migration of active hydrogen atoms. These results also indicated the initial formation of a Pd<sub>core</sub>–M<sub>shell</sub> (M represents Co, Ni, Cu, or Ru metal) structure, which finally forms HEA NPs via atomic diffusion with increasing reduction temperature, owing to the increase in configuration entropy.

A CoNiCuRuPd/TiO<sub>2</sub> catalyst synthesized in this manner exhibited high activity, different selectivity, and significantly improved stability compared with Pd/TiO<sub>2</sub> during the hydrogenation of CO<sub>2</sub>. Theoretical investigations also emphasized that the sluggish diffusion in these CoNiCuRuPd HEA NPs is caused by the combination of multiple metals, and that lattice distortion plays a crucial role in the superior robustness of this material. Further investigation to demonstrate the applicability of the present synthetic method is now under way.

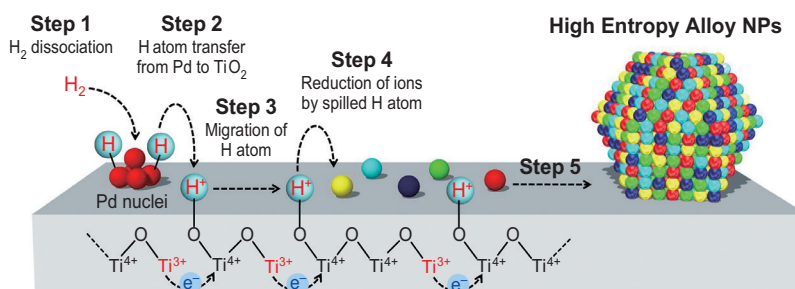


Fig. 2. Schematic illustration of the elementary steps in the formation of HEA NPs on a TiO<sub>2</sub> support assisted by hydrogen spillover.

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## References

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