

## Electronic Supplementary Information

### Tracking the Emergence of Epitaxial Metal–oxide Interfaces from Precursor Alloys

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#### Supplementary figures

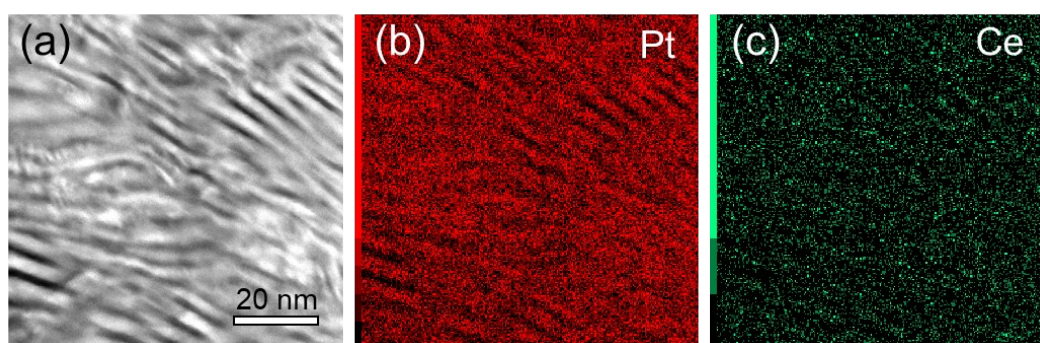


Figure S1. (a) HAADF-STEM image of Pt/CeO<sub>2</sub> nanocomposites and corresponding element distribution mappings of (b) Pt and (c) Ce. It suggests the bright and dark phases in (a) are rich in Pt and Ce, respectively.

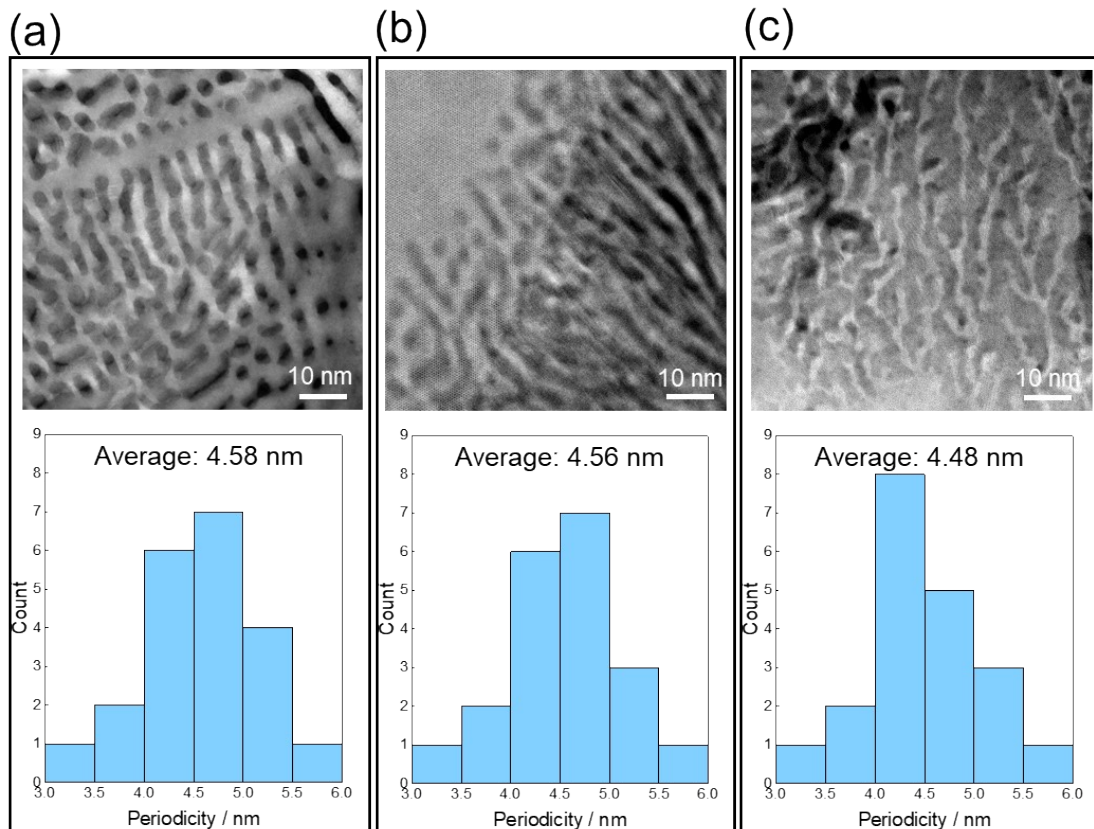


Figure S2. HAADF-STEM images of bulky powder Pt<sub>5</sub>Ce alloy annealed for (a) 12 h and (b) 30 min, and (c) firstly-FIB-thinned alloy annealed for 10 min. Bottom panels are the corresponding statistical data of the stripes periodicity in the alloys.

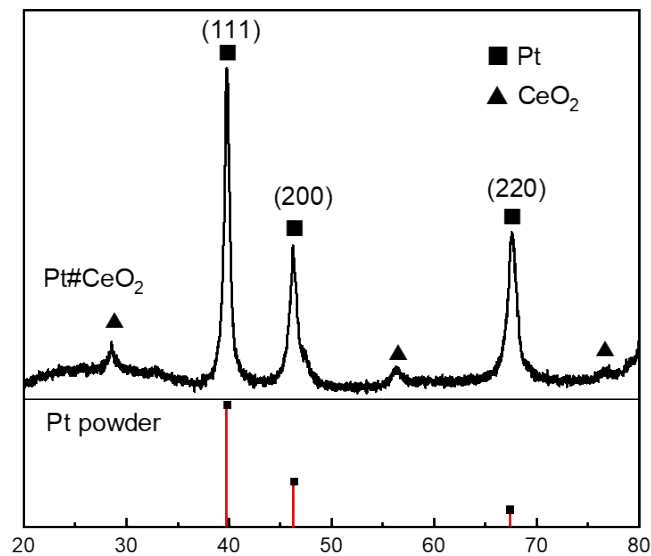


Figure S3. X-ray diffraction pattern of the Pt/CeO<sub>2</sub> composites and reference data of Pt metal, clarifying the strong relative intensity of the (220) plane.

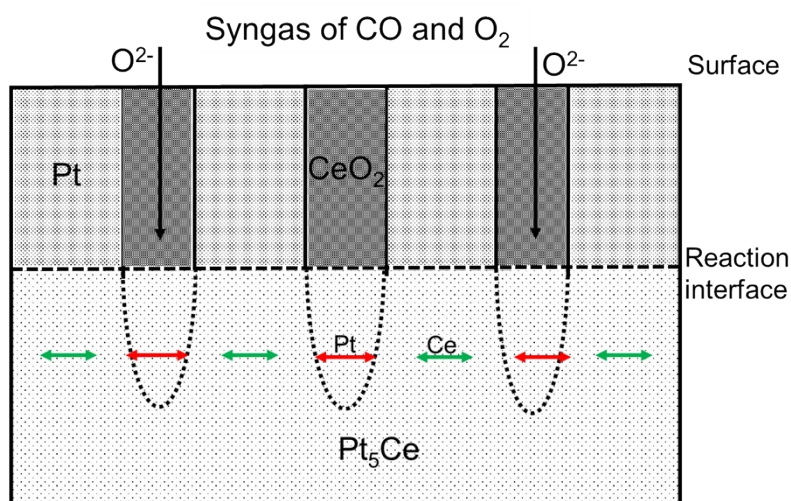


Figure S4. Schematic of the cross-sectional diffusion paths in the Pt<sub>5</sub>Ce alloy during phase separation. The vertical black arrows indicate the diffusion channels of oxygen from the surface. Red and green arrows indicate the diffusion paths of Pt and Ce atoms, respectively, in front of the phase separation area.

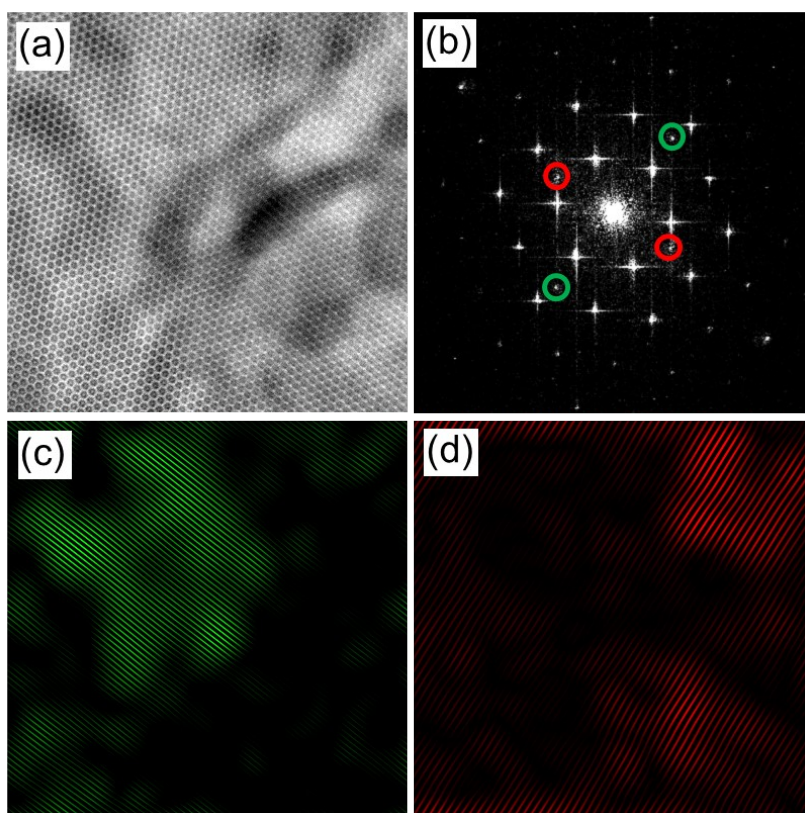


Figure S5. (a) HAADF-STEM image of Pt<sub>5</sub>Ce alloy annealed at 400°C, showing the segregation of Pt and Ce atoms; (b) corresponding FFT image of (a); (c) and (d) IFFT patterns extracted from the green and red circles in (b), respectively.

